



















# Basic Engineering Thermodynamics





# BASIC ENGINEERING THERMODYNAMICS

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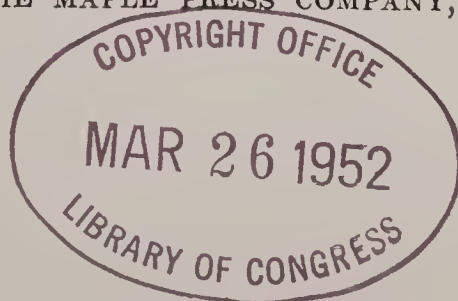
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## PREFACE

Thermodynamics is prerequisite to the specialized fields of engineering study. It may be designated as the key subject in the field of mechanical engineering, unlocking the door to more advanced courses. Because of its importance, many books are written on the subject of engineering thermodynamics. If these books are to be suitable for use as texts by the undergraduate engineering student, much of their content must consist of a rather conventional review of the principles of thermodynamics; the author can, at best, expect to contribute only occasional ideas and methods that are new.

The value of a new text in engineering thermodynamics should therefore be estimated with regard to factors other than novelty of treatment. The author of this text feels that the items in terms of which an appraisal should be made would include the following, not necessarily in the order of their importance.

1. *Selection of material.* Only an introduction to a subject as extensive as engineering thermodynamics can be accomplished in a book of a practical length for use as a text. Yet a foundation must be built for all of the specialized courses which are to follow, and a careful selection must be made to avoid an uneconomical use of the student's time.

2. *Continuity of treatment.* A selection of material having been made, the next requirement is that this material shall be so organized as to result in a continuous development of the main theme. The temptation to continue the development at hand beyond the point which is appropriate to the immediate purpose must be resisted in order to avoid distractions from the basic argument.

3. *Balance and consistency.* There are few authors who do not have their specialties within the broad field of engineering thermodynamics, and there is always a temptation to discuss these fields of special interest at greater length than is appropriate to the over-all purpose of the text. On the other hand, a tendency toward too brief and condensed a survey of topics of less interest to the writer must also be avoided.

4. *Rigor of treatment.* The development of thermodynamic concepts should be sufficiently rigorous to satisfy the student of the validity of the reasoning and convince him of the soundness of the argument. An undergraduate text may easily follow a line that is too rigorous, however, defeating its own purpose by presenting a proof that the average undergraduate student follows with difficulty, if at all.



5. *Readability.* The engineering student is inclined to resent a text which employs a style that, no matter how precise and rigorous are its arguments, requires that he spend too much time in rearranging and rephrasing its sentences and paragraphs into a form in which he can grasp their meanings. He is right, of course, for in analyzing the language used and in translating it into the form that makes sense to him, he may be distracted from the continuity of thought in which he should be encouraged.

6. *Clarity.* A simple and uncomplicated style of presentation is not the only requirement for clarity. In addition, the discussion of a given topic should be neither too condensed nor too extended. In this respect, the teacher of thermodynamics has a distinct advantage in writing on the subject. Through the years, the questions which his students have asked have told him what topics require more detailed and forceful presentation than would appear necessary on the basis of superficial examination, and he is thereby guided in the emphasis which he places upon these items. They will also have shown him when a numerical example will complement a general discussion of the topic to good effect.

The author of this text has had the objectives outlined above constantly in mind during the period of its compilation. He can only hope that those who read his book will feel that he has, in the main, attained them. The book has been designed as the basis of a two-semester course in engineering thermodynamics, a total of six to eight semester hours. By less intensive coverage and by eliminating certain parts, it may be used for a one-semester course. The treatment is such that the text is suitable for individual study, and the chapters not covered in classwork may be used for reference during later specialized courses and more advanced study. The author will welcome suggestions for the improvement of the book and notification of any errors that may be found.

In a few instances the method of approach differs from the usual. For example, the early identification of the ideal process as a maximum-work process and the use of the maximum-work principle as a tool throughout the book are a variation from the usual practice. The author has used this method in his classes and has found that it is a concept that makes sense to the student and is effective with him.

A full acknowledgment of credit is always impossible to the author of a book of this character. He has been influenced by his teachers, by the books he has read, by his students, by the texts from which he has taught. Credit is given specifically for the use of certain references at the points where the material has been introduced into this text. There are other places where the line of thought has been appropriated unconsciously and applied to the author's purpose. Special thanks are due Professor James H. Boggs of the faculty of the Oklahoma Agricultural and Mechanical

College for his assistance in reading and criticizing the manuscript, to Professor Bess Allen, Oklahoma Agricultural and Mechanical College, for her advice on matters of phrasing and English, and to the author's wife, Katherine, without whose understanding cooperation the writing of this book would have been a difficult task indeed. The author also wishes to thank Professor Emeritus Edwin F. Church, Jr. of the Polytechnic Institute of Brooklyn, whose especially able and constructive criticism of the manuscript has made it possible to correct and improve this text prior to its publication.

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## CHAPTER 1

### FUNDAMENTAL DEFINITIONS AND CONCEPTS

**1:1. Thermodynamics** is the science which is concerned with changes in the form or the location of energy. The subject is of special importance to the engineer since he deals with energy in large quantities.

The structure of thermodynamic theory is founded on the law of conservation of energy, which affirms that energy can be neither created nor destroyed and that structure would at once collapse if this law were shown to be invalid. Although the proof of the law is of a negative rather than a positive character (an instance has never been observed in which it did not hold), it is extremely unlikely that this foundation is not sound and solid; it has been time-tried and tested.

In general, the procedure in thermodynamic analysis consists in segregating a body of matter, called the *thermodynamic system*, which has the ability to receive, to store, and to release energy and in tracing it through the *thermodynamic process* that results as it changes its *state*. Attention is especially directed toward the amount and form of the energy that enters or leaves the system and to changes in the amount of energy stored in the system during the process. By the law of conservation of energy, the change in the stored energy of the system must derive directly from the energy which has been transferred across its *boundaries*.

**1:2. The thermodynamic system** is composed of a limited portion of matter and is defined in terms of the boundaries which enclose it. The two types of systems that are employed in thermodynamic theory are the *closed system* and the *open system*.

The boundaries of a closed system permit the passage of energy, but no matter may cross them. Thus the *mass* contained within these boundaries is constant<sup>1</sup> though the boundaries themselves may change their position to allow for changes in the volume or the shape of the system during a prescribed *change of state*. The state or condition of the closed system at a given instant is described in terms of its *properties*.

<sup>1</sup> Note that the *weight* is not constant if the gravitational constant  $g$  changes. It will be assumed throughout this text that the acceleration due to gravity is constant and that unit mass and unit weight may therefore be identical. The unit of mass we shall usually employ will be the pound, an amount of mass that, as the result of the earth's attraction, would *weigh* 1 pound; mass in terms of this unit will be denoted by the symbol  $M$ . Another unit of mass is the slug, which, under the standard acceleration of gravity, weighs 32.17 pounds. In terms of this unit, mass will be denoted by  $m$ ; thus  $M = m/g = m/32.17$ .

Energy that crosses the boundaries of a closed system will be classified as either *heat* or *work*. Heat is the form of energy which is transferred *from* external systems at higher temperature by reason of the temperature difference. The standard convention assigns the *positive* sign to heat that *enters* the system (owing to the system being at lower temperature than external systems) and the *negative* sign to heat *leaving* the system.

In thermodynamic usage, the term heat is restricted in its application to energy *crossing the boundaries of the system* solely by reason of a temperature difference between the system and external systems with which it is in communication. It is obvious that the state of the system might be so described as to prescribe a temperature difference between various parts of the system within its assigned boundaries. In that case the system is not in a state of *equilibrium*, and a tendency will exist toward a spontaneous exchange of energy *within the boundaries* due to this internal temperature difference. In the sense in which the term is used in thermodynamics, this exchange between parts of the same system does not constitute a flow of heat; it is rather to be considered a redistribution of stored energy. It is, of course, hardly necessary to state that stored energy in any form cannot properly be called heat. Heat is a transitory form of energy; energy cannot exist as heat. When heat leaves the system, we have, as evidence of its passage, an immediate increase in the stored energy of external systems; we may *observe* heat only in terms of the effects that its transfer produces. Heat is measured in quantity by its effects in terms of changes of stored energy as, for instance, by the change of temperature which it can produce in a given mass of a prescribed material.

The term work will undoubtedly recall to the mind of the reader the meaning of the word as used in mechanics. In mechanics, work was defined as that form of energy which resulted when a force moved through a distance and was measured as the product of the force and the distance it moved in its own direction. Thermodynamically, the term has both a broader and a narrower significance. Its meaning is broader in thermodynamics because it would include any form of transitory energy that might have as its *only* effect the type of work which we associate with mechanics. Thus the flow of electricity would be classified as work in the thermodynamic sense for we know from a study of electrical energy that it is, theoretically and in the limit, completely and continuously convertible to the work of mechanics.

On the other hand, the meaning of the term work is narrower in the thermodynamic sense, for, to be classified as work, it must *cross the boundaries of the system* in that form. This means that if a system expands it does work only if it meets and overcomes resistance from external systems; the amount of work performed is measured as the product of that



resistance and the distance (in its own direction) through which it is overcome. If a system is not in equilibrium, the pressure of its various parts may not be uniform and that part at higher pressure may expand, compressing the rest of the system; note that this is not work in the thermodynamic sense, for this energy does not cross the system boundaries. The standard convention gives the positive sign to work delivered by the body to external systems, the negative sign to work received by the system as, for example, when it is compressed.

An open system has boundaries which permit the passage not only of heat and work but also of matter. Thus the mass contained within those boundaries may change during a process. Also, the total change in the stored energy of an open system will depend not only upon the energy in the form of heat and work which has crossed its boundaries during the change of state but also upon the energy that crossed those boundaries in the form of stored energy in the matter which was introduced into or exhausted from the system during the same interval. However, this stored energy, though it crosses the system boundary, is not to be classified as *transitory energy*; heat and work are the only forms of transitory energy in the sense in which that word is used in thermodynamics. In the more common applications of the open system, new material is introduced at one or more points on the boundaries of the open system at exactly the same rate as it leaves at another point or points. In this special case the mass included within the system boundaries does not change although it is not composed of the same particles of matter.

The study of the thermodynamic process requires that the boundaries of the system must be accurately known. In later problems in this book, the extent of the system will often be defined by italicizing the words which describe its content.

**1:3. Stored Energy.** In order to understand the various forms in which energy may be stored in a system, it is necessary to set up some sort of concept as to the structure of the matter of which the system is composed. The kinetic theory of matter will be used for that purpose. But even if this theory, generally accepted as it is, were replaced by another, the structure of thermodynamic theory would not be endangered as long as the possibility of energy storage in matter, as implied in the law of conservation of energy, was not denied.

Matter is defined as that which has mass and occupies space. It may exist in the solid, the liquid, or the gaseous *phases*. As a solid the system has at least a certain amount of rigidity, a definite volume, and a distinctive shape which can be changed only by the application of appreciable force. The liquid assumes the shape of the vessel that holds it but retains a definite volume, being bounded by a free surface; it is compressi-



ble in only slight degree. A gas has neither shape nor volume of its own but fills any container in which it may be held; it is readily compressible.

According to the kinetic theory, the system is composed of very small particles called molecules. The number of these molecules is tremendous; for example, there are about  $5 \times 10^{20}$  molecules in a cubic inch of atmospheric air. But, in spite of their very large numbers, the individual molecule is so small that, even in the case of the solid, there are relatively large open spaces between them. Each molecule is attracted to every other molecule by a force which is analogous to the attraction between the planets of the solar system and which is inversely proportional to the square of their distance apart. It would seem that these attractive forces would ultimately draw the molecules of a system into a compact mass, but the individual molecule also has motion. This motion may be a translation or a rotation. In translation, the molecule travels through the voids between other molecules until it collides with another molecule, after which each travels off in a new direction at undiminished speed. Their speeds will vary with the weight of the molecule and with the temperature of the system and range upward to over a mile a second for hydrogen gas at ordinary atmospheric temperatures. The speed decreases with greater molecular weight and reduced temperature.

The molecule, in turn, is composed of atoms. A few molecules, the argon and helium molecules, for example, consist of only a single atom. Thus argon and helium are called monatomic gases. On the other hand, the number of atoms per molecule may be quite large. These atoms contain a heavy central nucleus with a positive charge of electricity about which negatively charged and extremely light electrons revolve.

The thermodynamic system as a whole may store energy in two forms; these are called *potential energy* and *kinetic energy*. Potential energy of the system is exemplified by the type of energy possessed by the water in an elevated tank due to its height above some datum level and is measured as the amount of work required to raise it to that elevation from the datum plane. Another example is the energy possessed by an extended spring due to the stresses set up in its material as it is lengthened; again the amount of potential energy of the spring is relative to some reference condition and is measured by the work the spring has received in extending it from the reference condition. The systems ordinarily encountered in engineering thermodynamics are of low density, and differences of elevation are so minor that the potential energy of the system may often be ignored with negligible error.

A system that is in motion possesses kinetic energy whether the motion is translational or rotational. Simple examples are a thrown ball, a flowing fluid, or a rotating flywheel. The second of these examples would be of more interest in engineering thermodynamics since the systems

employed are usually composed of liquids or gases and because instances of translational movement of the system *as a whole* are much more common than rotation. The translational kinetic energy of a system is a function of its mass and the square of its velocity. Velocity must be expressed with respect to some other system such as the surface of the earth, and the kinetic energy of the system is thus, like potential energy, a relative quantity. The kinetic energy of the system as a whole is readily and completely convertible to or from work, and its amount may be measured in terms of the work required to impart the given velocity to the system.

It was emphasized in the two paragraphs immediately above that we were discussing the stored energy of the system *as a whole* and that this form of stored energy was completely convertible into work. For purposes of easy reference, we shall hereafter often speak of the stored energy of the system as a whole, whether potential or kinetic, as *stored mechanical energy*.

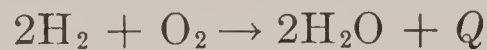
Stored mechanical energy does not take any account of the energy stored in the molecule because of its motion or its position with respect to other molecules. When the average distance between the molecules of a closed system is increased owing to an expansion of the boundaries of the system, an increase in the energy storage of this collection of molecules is indicated. This is analogous to the type of energy stored in a spring as it is extended (potential energy) but differs from it in an important respect. The pull between molecules is not concentrated in a single direction; each molecule has an attraction for other molecules on all sides of it. It might be considered an unorganized form of potential energy and certainly is one which is not readily convertible into work. We measure it ordinarily in terms of its thermal effects. In the case of gases, especially at low pressure and correspondingly large volume, the distance between molecules is relatively very much larger and the attractive forces between them correspondingly smaller. Accordingly, when a gas system changes its volume (but remains in the gaseous phase), there is very little *change* in *stored potential molecular energy*; in fact it may be possible to ignore *changes* in this form of stored energy altogether in dealing with this class of system. Of course this is not possible when the system changes its phase during the thermodynamic operation.

The velocity of the molecule, whether translational or rotational, represents stored energy analogous to the kinetic mechanical energy of a thrown ball, rotating in flight. But again this is an unorganized form of stored energy since the molecules are traveling in all directions. It is neither readily nor completely and continuously convertible to work and is measured in terms of its thermal effects, *e.g.*, in terms of the heat flow across the boundaries of the system which accompanies a change in the



amount of this form of stored energy. Again for purposes of ready reference, we shall speak of the stored energy of the molecule, whether potential or kinetic in character, as *stored thermal energy*. In the thermodynamic transaction, accent is placed on the *changes* of stored thermal energy that take place in the system rather than the absolute amount of energy stored in this form.

The engineer is often concerned with *combustion*. This is a type of *chemical reaction* during which, as the result of a new alignment of atoms and, at times, a change in the total number of molecules that constitute the system, energy is released. As an example, consider the union of two molecules of hydrogen, each composed of two hydrogen atoms ( $2\text{H}_2$ ), with one oxygen molecule, consisting of two atoms of oxygen ( $\text{O}_2$ ), to form two molecules of water, each comprising two atoms of hydrogen and one of oxygen ( $2\text{H}_2\text{O}$ ). The chemist would symbolize this reaction in the form



in which  $Q$  represents what he calls the “heat of reaction.” Recalling that in thermodynamics the term heat can never properly be used except as energy crosses the boundaries of a system, we observe that the expression heat of reaction must be used with care and understanding in engineering thermodynamics. To illustrate, let us suppose that the reaction which has been used as an example took place within a closed, rigid, non-conducting envelope. Although the mass of the matter contained within that envelope has not changed as the result of the reaction (the number of each kind of atom is the same in the products as in the reactants), there has been a reduction of one-third in the number of molecules since each molecule of the products contains three atoms instead of the two per molecule of each of the reactants. Because the envelope is rigid and nonconducting, no energy may pass the boundaries of the closed system contained within it. In the cited example, a small portion of the so-called “heat of reaction” may be absorbed owing to increasing the average distance between molecules. Even this is not always the case, for in some combustion reactions the number of molecules in the products may equal or even exceed the number in the reactants. Most of this energy must be taken up by an increased kinetic energy of the molecules, which means greater rates of molecular movement. It has already been noted that a higher temperature accompanies greater molecular velocities, and we may accordingly expect an increase of temperature. If now the envelope is made conducting (though still rigid), heat will pass outward across the boundary of the system because the temperature of the system is higher than that of its environment. Assuming that the environment is vast and thus capable of receiving this heat without change of temperature and



that the constant temperature of the environment is the same as the original temperature of the reactants, this passage of heat will continue until the temperature of the products is the same as the original temperature of the reactants. The total heat flow that takes place before this condition of equilibrium is reached is a measure of the *constant-volume heat of reaction*. A corresponding *constant-pressure heat of reaction*, based on the attainment of pressure as well as temperature equilibrium with the environment, is also of importance, but its discussion will be left for later coverage. It will be noted that, in order to bring the products back to the same temperature as the reactants, heat must leave the system—*negative* heat when the conventions of engineering thermodynamics are applied. In the equation as the chemist writes it, this heat is given a positive sign; the convention in regard to the sign of heat flow is thus, in the field of chemical thermodynamics, opposite to that which applies in engineering thermodynamics.

Once more for ready reference, when we wish to call attention to the possibility of the components of a system releasing energy through a chemical reaction such as that described above, we shall speak of the energy so released as *chemical energy*. Chemical energy is, of course, to be included in an inventory of stored energy, but as long as there is no change in the chemical form of the system, it can be disregarded in calculating the total change of stored energy of the system.

Energy may be stored in forms other than those discussed above. These would include magnetism, electricity, and capillarity. These forms of stored energy will not be discussed in detail at this time since they are of minor importance in engineering thermodynamics. Magnetism and electricity are both basically ascribed to the alignment of the positive and negative charges characteristic of the structure of matter. Capillarity is the ability of a liquid in a small tube to maintain a level above or below that of the liquid which surrounds the tube; it is due to that property of liquids which is called *surface tension*. It is because of surface tension that liquids can maintain a free surface.

**1:4. Properties of the System.** A *state* of a given system is its condition or its position with respect to other systems. A state is identified in terms of the properties of the system. Typical properties are the pressure, the volume, the temperature, the velocity, and the elevation of the system. All of these are, without doubt, observable characteristics which can be used to describe the state of the system at the instant of observation. The various forms of stored energy that have been discussed in the preceding article are, it would seem, also properties of the system since their magnitudes depend on characteristics of the system, like temperature, which have fixed values depending on the state. On the other hand, heat and work could not be classified as properties since they are forms in

which energy crosses the boundaries of the system; as a result of their passage a *change of state* could be expected. A change of state *may* take place, however, even if no work or heat flow are involved.

*Pressure* is the force exerted by a system on a unit area of its boundary. On the basis of the kinetic theory of matter it may be interpreted as the momentum of the molecules which strike that portion of the boundary in unit time. It is proportional to their mass and their velocity. Because of the very large number of these molecules it would seem that, for a finite system of uniform composition and uniform rate of molecular movement (temperature), the law of averages would assure that the pressure would be uniform over all segments of the boundary. This would be true except that, under the influence of gravity, the molecules above press down on those in the lower part of the system, compacting them so that a greater number strike a unit boundary area in unit time. The difference in pressure so created is quite small in the low-density systems of limited height that are of principal concern to the engineer, and it is the usual practice to neglect this effect of gravity in engineering thermodynamics.

Pressure is measured in units which are consistent with its definition as force per unit area, as pounds per square inch or pounds per square foot, for example. In this text these will be the units ordinarily employed, the symbol  $P$  being used if measurement in terms of pounds per square foot is intended,  $p$  for pounds per square inch. Pressure is sometimes conveniently measured in terms of the height of some fluid such as mercury; the pressure indicated in this case is that necessary to support a column of the fluid of the given height under the influence of gravity. The equivalent pressure is the product of the density and the height, or  $P = wz$ . The pressure equivalent to a column of mercury one inch in height is 0.491 psi.

The nomenclature of pressure includes the terms absolute zero of pressure, atmospheric pressure, gage pressure, absolute pressure, and vacuum. *Absolute zero of pressure* is found in a space in which there is no molecular momentum, owing either to the absence of molecules or to the absence of molecular motion; it is therefore characteristic of a void and may be thought of as the pressure at the top of the earth's atmosphere. *Atmospheric pressure* is due to the weight of the earth's atmosphere and varies with altitude and with weather conditions. *Standard atmospheric pressure* is equivalent to a barometric height of 29.92 in. Hg (or 14.7 psi) and represents the average atmospheric pressure at sea level.

Pressure-measuring devices measure differences in pressure and, in engineering practice, frequently the difference between the pressure of the system and that of the atmosphere. A pressure gage on a boiler, for example, gives the difference between the pressure of the steam on the inside and the atmosphere on the outside of the boiler, and this difference



is called the *gage pressure*. Gage pressure may be defined as the pressure in excess of that of the atmosphere, and the corresponding *absolute pressure* may be obtained by adding the atmospheric pressure to the gage pressure. A pressure less than atmospheric pressure is called a vacuum and may be recorded on a gage or in terms of the height of a fluid column. *Vacuum* is the amount by which the pressure is less than the pressure of the surrounding atmosphere; the corresponding absolute pressure is found by subtracting the vacuum from the atmospheric pressure.

The *temperature* of a system measures its capacity for transferring heat to other systems. If the temperature of those external systems becomes equal to that of the system, the transfer of heat ceases; this does not, however, preclude the transfer of energy in the form of work. Based upon the kinetic theory of matter and the method by which energy is stored in the molecule (see Art. 1:3), temperature may be defined as a measure of the kinetic energy of the molecule. In the case of gases at low pressure, for which changes in potential molecular energy are negligible, the change of temperature may account for the total change in the stored energy of the molecules of which the system is composed. It would not account, however, for changes in other forms of stored energy such as stored mechanical energy. Nor would a unit change in temperature necessarily represent the same change in stored kinetic molecular energy at all temperature levels.

A rise in the temperature of a system is an unfailing indication that its molecules have increased velocity, but equality of temperature between two bodies, as evidenced by the fact that there is no change in any observable characteristic when they are placed in communication such as would result from a flow of heat, does not necessarily mean that the velocity of their molecules is the same unless the molecules of the two systems have equal mass.

Temperatures are often measured by bringing a carefully calibrated external system into communication with the system whose temperature is to be ascertained and allowing equilibrium to be established between the two. The effect on the properties of the calibrated system is then observed and interpreted in terms of the common temperature of the two systems. The effects that are commonly used for the measurement of temperature in these calibrated systems, which have the general name of *thermometers*, include the change in volume of a solid, a liquid, or a gas while the pressure is constant, the change in pressure of a gas at constant volume, the change in vapor pressure of liquids, and the change in electrical resistance. Other methods are based on the thermoelectric properties (the principle of the thermal couple) or on the amount of radiant energy emitted (the optical pyrometer). No one method of temperature measurement is practical over the complete range of temperatures.



Scales of temperature may be entirely arbitrary. Two scales in common use are the centigrade and the Fahrenheit. On any scale of temperature there are certain “anchor points” which are used to orient a reading on that scale and make possible its comparison with standard levels of molecular activity and with temperatures on other scales. On the centigrade scale the zero point corresponds to the temperature of equilibrium between ice and water under a pressure of 1 standard atmosphere (the melting temperature of ice at that pressure), and a temperature of 100 deg on the centigrade scale denotes a temperature level at which water and steam are in equilibrium under the same pressure of 1 standard atmosphere (the boiling temperature of water at that pressure). There is thus a spread of 100 deg of centigrade temperature between these two points. On the Fahrenheit scale the first of these points is assigned a temperature of 32 deg, the second falls at 212 deg, a temperature difference of 180 Fahrenheit degrees. Thus the change of temperature represented by 1 deg on the centigrade scale is equivalent to that denoted by  $\frac{9}{5}^{\circ}\text{F}$ . For conversion of temperatures on either of these two scales to equivalent temperatures on the other, the following formulas will be found convenient:

$$\text{Degrees centigrade} = \frac{5}{9}(\text{degrees Fahrenheit} - 32) \quad (1:1)$$

$$\text{Degrees Fahrenheit} = \frac{9}{5}(\text{degrees centigrade}) + 32 \quad (1:2)$$

For the purpose of measuring temperatures which are well above or below the range of ordinary atmospheric temperatures, other anchor points are desirable. These were selected in 1927 as the result of international agreement and form the basis of the *international scale of temperature*. In addition to the two that were cited above, international recognition was given to the boiling point of oxygen ( $-182.97^{\circ}\text{C}$ ), the boiling point of liquid sulfur ( $444.60^{\circ}\text{C}$ ), the melting point of solid silver ( $960.5^{\circ}\text{C}$ ), and the melting point of solid gold ( $1063^{\circ}\text{C}$ ); all of these points correspond to a pressure of 1 standard atmosphere.

Standard methods of evaluating intermediate temperatures were also adopted by action taken at this international conference. These methods are based on the use of electrical-resistance devices up to a temperature of  $660^{\circ}\text{C}$ , the use of a thermal couple between that temperature and the gold point ( $1063^{\circ}\text{C}$ ), and, above the gold point, by means of an optical pyrometer.

The zero points on the centigrade and Fahrenheit scales of temperature have been selected arbitrarily; temperatures may be demonstrated that are represented as negative temperatures on both scales. As will be shown later, there is a level of temperature below which it is impossible to go; this temperature would correspond, according to the molecular theory, to an absence of molecular movement. This level is called *absolute zero*

of temperature. On the centigrade scale it is located at  $-273.16$  deg, on the Fahrenheit at  $-459.69$  deg. These values are approximate and must be deduced since, again as will be shown later, absolute zero of temperature cannot be attained. The boiling point of water at standard atmospheric pressure would thus be located at  $373.16$  deg on a scale of temperature that had its zero point at absolute zero and was laid off in centigrade degrees. The same point would be represented by a temperature of  $671.69$  deg on a similar scale of temperature which was subdivided into Fahrenheit degrees. Both of these are called *absolute scales of temperature*, and temperatures as measured on them are called *absolute temperatures*. It is customary to refer to absolute temperatures measured in centigrade degrees as *degrees Kelvin* ( $^{\circ}\text{K}$ ) and, as measured in Fahrenheit degrees, as *degrees Rankine* ( $^{\circ}\text{R}$ ). Scalar temperatures on either the centigrade or the Fahrenheit scale will be denoted by the symbol  $t$ , absolute temperatures by  $T$ . Thus the relation between degrees Rankine and degrees Fahrenheit is given by

$$T = t + 459.69$$

In slide-rule calculations it is usual to substitute the value 460 for 459.69 in this equation.

The total *volume* ( $V$ ) of a system is the space that it occupies; the specific volume ( $v$ ) is the space occupied by a unit mass. When the specific volume varies throughout a system, as is the case under the influence of gravity or when the system is a mixture of phases, its value must be defined, with respect to a given point in the system, as the space occupied by an infinitesimal part of the system divided by the mass of that infinitesimal part. *Density* is the reciprocal of specific volume.

In the course of the development of thermodynamic theory it will be necessary and desirable to introduce properties other than those which have been discussed in the preceding paragraphs. Some others which will occur to the reader are elevation, velocity, electrical resistance, and viscosity. The pressure, volume, and temperature are the properties that are most commonly used in describing the state of the system and might be called the primary properties. *Equations of state* for the various materials of which systems are composed ordinarily show the relationship between these primary properties.

Properties may be classified as *extensive* and *intensive*. The value of an extensive property which applies to a given system depends on the mass of that system; the total volume and the total stored energy of the system are examples of extensive properties. Pressure, temperature, elevation, velocity, electrical resistance, and viscosity are intensive properties; their values for the system as a whole are not the sums of the corresponding values for the various parts of which the system is composed.



The identification of a quantity which is associated with a system as a property of that system is often important. For this purpose it will be remembered that, whenever a system returns to a given state, all of its properties must have their original values. Furthermore, when a system changes its state, the change of any property will depend only on the end states and not at all upon the means by which the change of state was accomplished.

**1:5. The Pure Substance and the Simple System.** The pure substance is homogeneous in composition and in chemical form and retains its chemical identity. A mixture of liquid water and steam would satisfy these requirements and would be classed as a pure substance even though the density is not uniform throughout the mixture. Dry air would ordinarily be a pure substance although it is a mixture of gases. However, at temperatures low enough to bring about a partial condensation of its constituents, it would be found that the percentage of the more volatile components would be lower in the liquid than in the gases of the resulting two-phase mixture; as a mixture of two phases, air is not a pure substance. Atmospheric air is a pure substance only as long as there is no condensation of its water vapor content. A mixture of hydrogen and oxygen in the gaseous phase is classified as a pure substance; when the two gases unite chemically to form water vapor, a different pure substance results.

The importance of the thermodynamic concept of a pure substance lies in the fact that, in the absence of motion, gravity, capillarity, magnetism, and electricity, all properties of a system composed of the substance are established if only two, which are independent of each other, are known. If these two properties are used as the coordinates of a graph and if the known values of the two properties that correspond to a given state of the pure substance are used to locate a point on the graph, the position of that point also fixes the values of all other properties associated with that state. Thus it is possible to write an *equation of state* for the pure substance which will express any property in terms of not more than two other (and independent) properties. A partial list of the properties for which such equations can be written includes pressure, temperature, specific volume, stored molecular energy, density, viscosity, and electrical resistivity. Many others will later be added to this list.

It is noted that the two properties which are to be the coordinates of the graph must be independent of each other. The pressure and the volume, for instance, are often used and have a special usefulness to be developed later. Mutually dependent properties, such as specific volume and density, could not be used for obvious reasons. For mixtures of phases, the pressure and temperature of the pure substance are interdependent and could not be used although, for any single phase, they would serve.



The only form of stored energy of which the relative value could be expressed in the form of an equation of state for a given pure substance is stored molecular energy, to which we shall hereafter apply the name *internal energy* and which we shall designate by the symbol  $U$  for total,  $u$  for specific internal energy. The attention of the reader is called to the fact that all forms of stored energy, including the kinetic and potential energy of the system as a whole (stored mechanical energy), are, in the broad sense, internal energy and that that term (though not the symbol  $U$ ) as used in many texts includes them. In this book, for purposes of clarity, the sum of all forms of stored energy will be called *stored energy*

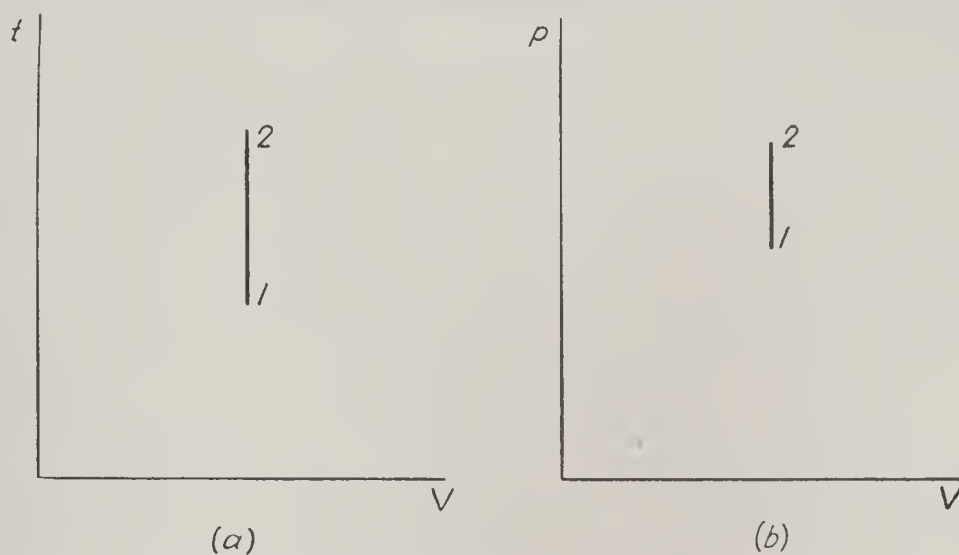


FIG. 1:1. The constant-volume path.

and will be represented by the symbol  $E$  for total,  $e$  for specific stored energy. These symbols are those conventionally employed to designate stored energy in general.

The simplest type of system with which it is possible to deal consists of a pure substance, the effects of motion, gravity, capillarity, magnetism, and electricity being either absent or negligible in amount. Since it is *changes* in the amount of stored energy that are of principal concern and since, by definition of the pure substance, the stored energy due to chemical form does not change,  $\Delta e = \Delta u$ . Indeed, the forms of stored energy that are either present in negligible amount or do not change in amount as the state of the system changes are usually ignored, and the internal energy represents the total stored energy, or  $e = u$ .

The system is only slightly less simple when the effects of motion and gravity are included, as is often the case for open-system analysis. In this case,  $e$  may be obtained by adding to  $u$  terms which represent the amount of additional energy storage due to these two effects.

**1:6. The state path** is the succession of states through which the system passes as it changes its state. Consider a simple gas system confined in a closed rigid shell. The condition of this system originally is represented by the position of point 1 on Fig. 1:1a; here the coordinates are tempera-

ture and volume. If heat is supplied to the system and passes inward across its boundaries, the temperature will rise and the *path* 1-2 will be traced. Any point on this path will represent an intermediate state of the system at which not only the temperature and volume but all properties of the system will have fixed values. Thus the same state path may be represented, as in Fig. 1:1b, on coordinates of pressure and volume; in fact, any pair of independent properties of the system could be utilized for this purpose.

The path followed in this example is described as a constant-volume path. Other special kinds of state paths which will suggest themselves to the reader on the basis of properties already defined are those of con-

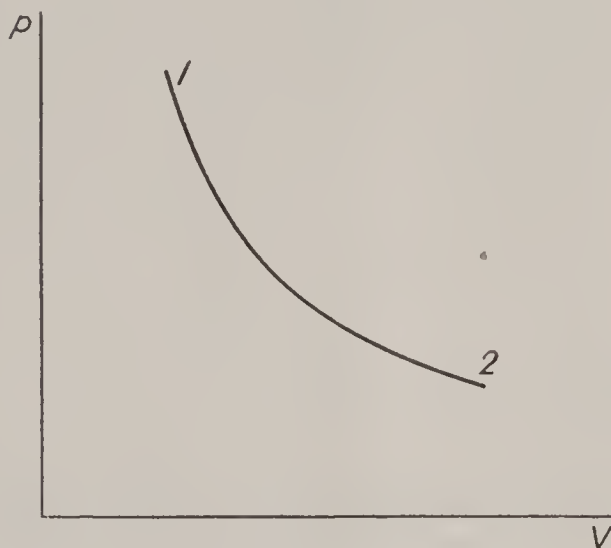


FIG. 1:2. Graphical description of a state path.

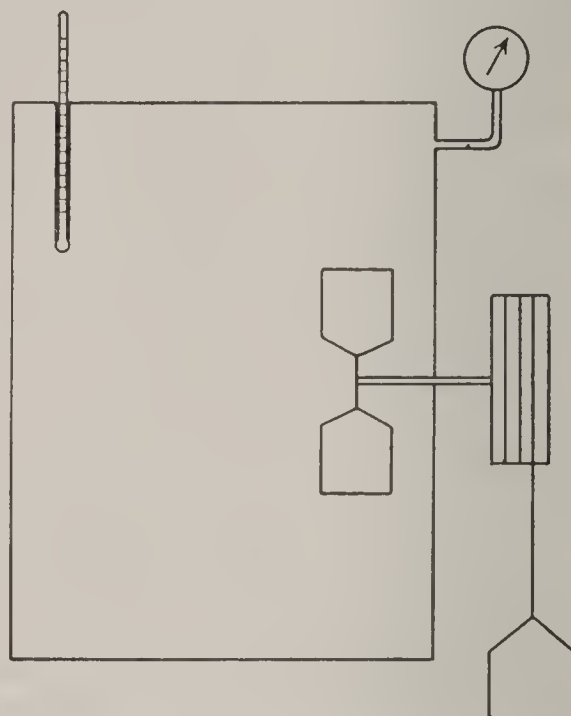


FIG. 1:3. The paddle-wheel process.

stant pressure, constant temperature, and constant internal energy. Whenever any property is constant during a change in state and the end states are known, the state path for a given simple system is completely defined for any pair of coordinates that represent independent properties of the system. The same is true, of course, when no property is constant but the path is described in terms of the change in properties. The description in this case may be graphical as indicated in Fig. 1:2.

**1:7. The Process.** A description of the thermodynamic process involves not only a description of the path but also the method by which the path was followed. For example, the path illustrated in Fig. 1:1 was ascribed as due to the passage of heat across the system boundaries. The same path could have been followed if the energy that crossed the boundaries of the system had been in the form of work. This possibility is illustrated in Fig. 1:3, in which a paddle wheel, driven by an external agency, stirs the confined system and thereby increases its temperature; this is a variation of a fundamental experiment in elementary physics.



Thus the same *path* may be followed during either a no-work or a no-heat process. An infinite variety of heat-work combinations are possible for every state path.

Processes which take place without heat flow are called *adiabatics*. The description of a process as an adiabatic does not define the path, even if the end states are known, unless some hint is given as to the rate at which work crosses the boundaries of the system during the process.

**1:8. The Cycle.** Any path or process whose end states are identical is called a *cycle*. However, the description of a cycle is not thermodynamically complete unless it is described in terms of the process or processes traversed during the cycle. In Fig. 1:1 a cycle is formed if the state of the system is returned to that represented by point 1. This may be done by inducing heat to flow out of the system; the path followed during the original process is exactly retraced, but if the increase of system temperature during the process 1-2 was due to work supplied the system rather than heat flow, the same cannot be said of the process. Note also that whereas the path 1-2 can be followed without any heat flow whatever the return passage, 2-1, must involve the flow of heat; the paddle-wheel process cannot be reversed to cause work *alone* to flow out of the system.

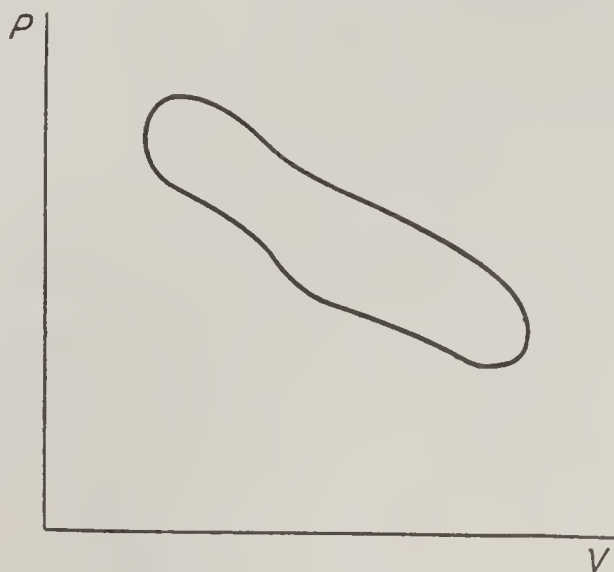


FIG. 1:4. The cycle.

If the path 1-2 in Fig. 1:1 represents a process involving no work, the heat flow outward during the return to state 1 is equal to the heat received as the temperature of the system increased; the net heat flow for the cycle is thus zero or  $\oint dQ = 0$ . On the other hand, if heat flow is involved only in the return process,  $\oint dQ < 0$ . Similarly as regards the net work of the cycle, in the first instance  $\oint dW = 0$  and, in the second,  $\oint dW < 0$ .

It is not intended to imply that the cycle always consists of a direct reversal of a state path; the more usual (and more useful) form of cycle has a state path which encloses an area as shown in Fig. 1:4.

**1:9. Identification of a Property.** It is sometimes necessary to establish whether a quantity associated with a given system is a property of that system. If it is a property, it may be used as a coordinate in plotting a state or a path of the system and its change may be computed for any process as based on the end states alone without regard for the manner in which the change of state was effected. It is this characteristic of a property which makes possible its identification.



In traversing a cycle a return is always made to the starting point. This is an identical state with identical properties, and therefore, if it can be shown that the total change of the quantity around any and all cycles which the system can be caused to traverse is zero, that quantity is established as a property of the system. Conversely, if any cycle can be found for which the line integral of the quantity is not equal to zero, it cannot be classified as a property. A brief review of Art. 1:8 will indicate that heat and work, at least as they are considered individually, are *not* properties.

If a quantity is expressed entirely in terms of the whole value (rather than the changes) of known properties of the system, it is identifiable as a property of that system; such properties are called *composite properties*.

It will be remembered that a simple system has only two independent properties and that any third property may be expressed in terms of these two. The equation that connects the three represents a three-dimensional surface for which the coordinates are, respectively, the three properties. Thus, if  $x$  and  $y$  are the independent properties and  $P$  is the dependent property,

$$P = f(x, y) \quad (1:3)$$

$$dP = \frac{\partial P}{\partial x} dx + \frac{\partial P}{\partial y} dy = M dx + N dy \quad (1:4)$$

If  $P$  is a function of  $x$  and  $y$ , as it must be if it is a property, its second derivative with respect to  $x$  and  $y$  is

$$\frac{\partial^2 P}{\partial x \partial y} = \frac{\partial}{\partial y} \left( \frac{\partial P}{\partial x} \right) = \frac{\partial}{\partial x} \left( \frac{\partial P}{\partial y} \right) \quad \text{or} \quad \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \quad (1:5)$$

That is, the order of differentiation is unimportant. If this requirement is satisfied,  $M dx + N dy$  is called an *exact* differential. If, on the other hand,  $P$  is not a property (though its amount may be expressed in the form  $M dx + N dy$ )  $\frac{\partial M}{\partial y}$  is not equal to  $\frac{\partial N}{\partial x}$ . This furnishes another means by which a property may be identified.

**1:10. The Equation of State.** The substance of which the simple system is composed retains its chemical identity, and, as has been previously stated, it has, in the absence of motion, gravity, capillarity, magnetism, and electricity, only two independent properties. For ease of reference, it will be called a pure substance though the use of that term should not be understood to imply that the pure substance may not consist of a mixture of component substances. However, if a mixture, the proportions of its components must be uniform throughout the pure substance. Any property of the pure substance may be expressed in terms of not more than two other properties, and the equation which results will

represent a surface. This equation, it will be remembered, has been called an equation of state. One of the simplest examples of an equation of state is that which applies to an ideal gas and connects the pressure, volume, and temperature; it will be developed in a later chapter but is introduced at this point to aid our discussion.

$$pv = CT \quad (1:6)$$

in which  $C$  is a constant that varies with the gas and  $p$  is the *absolute* pressure. That  $C$  is not a *dimensionless* constant will be evident if the dimensions of the product  $pv$  are compared with those of  $T$ ; its value will change if, for instance, the pressure unit is changed from pounds per square inch absolute to pounds per square foot absolute. Equations of state are ordinarily much more complicated in their form than Eq. (1:6), and it is seldom possible to write the same equation to fit both of two phases accurately. That need not concern us for the present; more general equations of state will be discussed in a later chapter.

Equation (1:6) is only one of a number of equations of state which apply to the ideal gas; it connects the primary properties. It will be shown later that another relationship, based directly upon and following from Eq. (1:6), is

$$u = A + Bpv \quad (1:7)$$

in which  $A$  and  $B$  are constants though, since they are not dimensionless, they will change in value for a given pure substance as  $u$ ,  $p$ , and  $v$  are expressed in varying units. Again it should be emphasized that this is not a general form for the calculation of the internal energy of all pure substances.

*Example 1:10.* For a certain pure substance, Eqs. (1:6) and (1:7) are adequate as the corresponding equations of state if  $A = 16$ ,  $B = 0.46$ , and  $C = 0.37$  when  $p$  is measured in pounds per square inch absolute,  $v$  in cubic feet per pound,  $T$  in degrees Rankine, and  $u$  in Btu per pound. (The Btu, or British thermal unit, is a unit of energy that will later be defined. It approximates in magnitude 778 ft-lb.) A system consisting of 3 lb of this substance is confined in a rigid shell at a pressure of 50 psig and a temperature of 60°F. Heat is supplied the system, and, as a result, its temperature increases to 120°F. Calculate (a) the internal volume of the container, (b) the final pressure of the system, and (c) the change of internal energy which resulted from the process.

*Solution:*

$$(a) \ v_1 = \frac{CT_1}{P_1} = \frac{0.37(460 + 60)}{50 + 14.7} = 2.97 \text{ ft}^3/\text{lb}$$

$$V_1 = Mv_1 = (3)(2.97) = 8.91 \text{ ft}^3$$

$$(b) \ v_2 = v_1 = 2.97 \text{ ft}^3/\text{lb}; \ T_2 = 120 + 460 = 580^\circ\text{R}$$

$$p_2 = \frac{CT_2}{v_2} = \frac{(0.37)(580)}{2.97} = 72.2 \text{ psia or } 57.5 \text{ psig}$$



$$\begin{aligned}
 (c) \quad u_1 &= A + Bp_1v_1 = 16 + (0.46)(64.7)(2.97) = 104.5 \text{ Btu/lb} \\
 u_2 &= A + Bp_2v_2 = 16 + (0.46)(72.2)(2.97) = 114.7 \text{ Btu/lb} \\
 u_2 - u_1 &= 114.7 - 104.5 = 10.2 \text{ Btu/lb} \\
 U_2 - U_1 &= M(u_2 - u_1) = (3)(10.2) = 30.6 \text{ Btu}
 \end{aligned}$$

### Problems

1. Classify any of the following which are properties as intensive or extensive: work, kinetic mechanical energy, modulus of elasticity, mass, moment of inertia, coefficient of linear expansion, color, stress (in a solid system), surface tension (in a liquid system).

2. A ton of gold is shipped from Alaska, where  $g = 32.22$ , to San Francisco, where  $g = 32.15$ . What is its weight in San Francisco? What is the mass of the gold in Alaska? In San Francisco?

3. Convert the following pressures to pounds per square inch absolute. Barometer = 29 in. Hg (a) 3000 psfa; (b) 25 psig; (c) 27 in. Hg vacuum; (d) 2000 psfg.

4. Convert the following pressures to pounds per square foot gage. Barometer = 30 in. Hg. (a) 1400 psig; (b) 1000 psfa; (c) 20 in. Hg vacuum; (d) 150 psia.

5. Change the following temperatures to degrees Rankine: (a) 400°F; (b) -5°C; (c) 220°K.

6. Change the following temperatures to degrees Fahrenheit: (a) 440°R; (b) 15°C; (c) 260°K.

7. Devise a means of measuring temperature (a thermometer) which employs principles not ordinarily made use of in thermometers. Explain how you would calibrate your device.

8. Five pounds of air occupies a total volume of 60 cu ft. What is the weight density of the air? Its mass density in slugs per cubic foot?

9. In the description of each of the following processes, the system is defined by the italicized words. In each case (1) state whether the system is an open or a closed system and (2) whether it is a simple system. (3) Determine whether the heat flow that accompanies the process is positive, negative, or zero. (4) Do the same for the work of the process.

(a) A container with rigid nonconducting walls holds *air* and an electric heating element, which is connected to a source of power external to the container. The temperature and pressure of the air increase.

(b) A container with rigid nonconducting walls holds *air* and an *electric heating element* which is connected to a source of power external to the container. The temperature and pressure of the air increase.

(c) A container with rigid nonconducting walls holds *air* and an *electric heating element with connected storage battery*. The temperature and pressure of the air increase.

(d) A teakettle with its *contents of water, water vapor, and air* is placed on a stove. As the result, steam at atmospheric pressure issues from the spout.

(e) A vessel with rigid nonconducting walls is divided into two compartments by a rigid nonconducting partition. One of the compartments is filled with *air*; the other is a void, containing no matter. The partition is removed, and the air expands to fill the larger space.

(f) *Air* is confined in a cylinder with rigid nonconducting walls and head but fitted with a gastight piston, also nonconducting. The pressure of the air inside the cylinder is less than that on the outside face of the piston, and the piston moves, compressing the charge of air.

(g) *Steam* flows through a turbine with nonconducting walls, turning the turbine shaft against the resistance offered by an electric generator.



(h) *Water* enters a boiler, and *steam* leaves it, both at the same pressure; the specific volume of the steam is greater than that of the water.

(i) A *mixture of hydrogen and oxygen* at atmospheric pressure and temperature in the proper proportions for complete combustion is confined within a rigid nonconducting pressure vessel. A spark, which may be considered negligible, ignites the mixture.

(j) Same as (i) except that the walls of the vessel, though rigid, are conducting. The process ends when temperature equilibrium with the atmosphere is again established.

(k) Same as (i) except that the walls of the container are both flexible and conducting; they do not rupture. The process ends when temperature and pressure equilibrium with the atmosphere is again restored.

10. A closed system traces a cycle of operations. Which of the following are necessarily true statements? (a)  $\oint dQ = 0$ ; (b)  $\oint dQ > 0$ ; (c)  $\oint dQ < 0$ ; (d)  $\oint dP = 0$ ; (e)  $\oint dP > 0$ ; (f)  $\oint dP < 0$ ; (g)  $\oint dW = 0$ ; (h)  $\oint dW > 0$ .

11. In the following expressions,  $P$ ,  $v$ ,  $s$ , and  $T$  are properties, and  $a$ ,  $b$ ,  $n$ ,  $R$ ,  $J$ , and  $C$  are constants. In which cases is  $X$  a property of the system? When  $X$  is found to be a property, write an expression for it in terms of other properties and the appropriate constants.

(a)  $dX_1 = T \, ds - \frac{P \, dv}{J}$

(b)  $dX_2 = P v^{n-1} \, dv + v^n \, dP$

(c)  $dX_3 = \frac{C \, dT}{v} - \frac{CT}{v^2} \, dv$

(d)  $dX_4 = \frac{R \, dT}{v - b} - \left[ \frac{RT}{(v - b)^2} - \frac{2a}{v^3} \right] dv$

(e)  $dX_5 = \frac{R \, dT}{v} + \frac{RT}{v^2} \, dv$

At the end of the earlier chapters of this text, a number of problems will be stated the solutions of which will be based on the use of the equation of state of an ideal gas, following the form of Eqs. (1:6) and (1:7). Four gases will be used, and these, for convenience, will be designated as gas *W*, gas *X*, gas *Y*, and gas *Z*. In the table below the values of the constants  $A$ ,  $B$ , and  $C$  in Eqs. (1:6) and (1:7) are tabulated for each. The stated values of the constants as given in the table are based on  $p$  in pounds per square inch absolute,  $v$  in cubic feet per pound,  $T$  in degrees Rankine, and  $u$  in Btu per pound. It will be observed that gas *Y* is the gas used in Example 1:10.

Const	Gas <i>W</i>	Gas <i>X</i>	Gas <i>Y</i>	Gas <i>Z</i>
<i>A</i>	14.7	854	16.0	71.0
<i>B</i>	0.639	0.570	0.460	0.282
<i>C</i>	0.244	0.596	0.370	2.68

12. At standard atmospheric pressure and a temperature of 32°F, what is the specific volume of (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

13. The density of a gas is 0.1 lb/ft³ at a temperature of 50°F. Under what pressure is it confined if it is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

14. A gas is confined under a pressure of 5 atm abs, and its specific volume is 5 ft³/lb. What is its temperature in degrees Fahrenheit if it is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

15. What is the internal energy of a 5-lb gas system at atmospheric pressure and a temperature of 100°F if it is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ ?

16. What is the rate of change of specific internal energy with respect to temperature for (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ ?

17. Show that the coefficient of cubical expansion (the rate of increase of volume per unit increase in temperature) at constant pressure is the same for all four gases at the same temperature. What is its value at 100°F?

18. Assume that the state path shown in Fig. 1:2 represents an isothermal (constant-temperature) expansion and that  $p_1 = 120$  psia,  $t_1 = 300^\circ\text{F}$ , and  $V_1 = 1$  ft<sup>3</sup>. What weight of gas takes part in the expansion if it is (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ ? Write the equation of the state path, and show that it will be the same for all of the gases.

19. One pound of a gas begins an isothermal expansion at  $p_1 = 120$  psia,  $t_1 = 300^\circ\text{F}$ . Write the equation of the state path if the gas is (a) gas  $W$ , (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ . Show the relative position of these state paths on the same  $pv$  diagram.

### Symbols

$A, B, C$	constants
$e$	stored energy of a system of unit mass in general
$E$	stored energy of a system in general
$g$	acceleration due to gravity
$m$	mass, slugs
$M$	mass, lb; also, weight
$p$	pressure, psi
$P$	pressure, psf; also, any dependent property
$Q$	heat flow
$t$	scalar temperature
$T$	absolute temperature
$u$	energy stored as thermal energy in a system of unit mass
$U$	stored thermal energy of a system
$v$	volume of a system of unit mass, specific volume
$V$	volume of a system
$w$	density
$W$	work
$x, y$	any two independent properties
$z$	height, elevation above a reference level

## CHAPTER 2

### THE FIRST LAW AND THE CLOSED SYSTEM

**2:1. The First Law of thermodynamics** is a statement of the implications of the law of conservation of energy in a form that is specifically designed for direct application to the development of thermodynamic theory. It may be stated, in one of its many variations, as follows:

*When any system is carried through a process or series of processes that eventually return it to its original state, the net amount of heat flow into the system is equal to the net amount of work delivered to external systems during the cycle.*

The only proof of this law is the failure of all attempts to prove it false. Because of those failures we have confidence in its validity and are content to use it as a part of the foundation on which the structure of thermodynamic theory will be built.

The First Law makes some progress in that direction immediately possible since, taken in conjunction with its parent law, the law of conservation of energy, it confirms the concept of stored energy as a property of the system. For when the system has returned to an identical state at which it must have identical properties, as was the result after its traversal of a cycle, the First Law states that in passage around that cycle no net energy could have been transferred to or from the system. Since energy can neither be created nor destroyed, the amount of energy stored in the system must be the same at the end of the cycle as at the beginning. This is an application of one of the methods suggested for the identification of a property in Art. 1:9.

The various forms of energy are ordinarily measured in different units. For instance, we usually contemplate the measurement of heat in British thermal units, of work in foot-pounds; in tables of properties, internal energy is stated conventionally in Btu. Interpreting the meaning of the First Law as it applies to these units of energy, it is seen that a fixed relationship must exist between them. Stated in somewhat different fashion, it is entirely practicable to express heat flow quantitatively in terms of foot-pounds and work in Btu.

The British thermal unit (Btu) was originally defined as  $\frac{1}{180}$  of the amount of heat necessary to raise the temperature of one pound of water from the freezing point (32°F) to the boiling point (212°F) under a constant pressure of one atmosphere. The same international conference



that established the international scale of temperature to which reference was made in the preceding chapter, recognizing that the measurement of heat was inherently less precise than the measurement of work, redefined the Btu as the equivalent of 778.2 ft-lb of energy. This ratio corresponds, according to recent experimental data, to a unit of energy very slightly smaller than was described in the original definition of the Btu.

It will be our policy to measure heat flow and internal energy in Btu and to measure work in foot-pounds. The relation between these units is  $1 \text{ Btu} = 778.2 \text{ ft-lb}$  and will be symbolized by a proportionality factor  $J (= 778, \text{ approximately})$ . Thus the First Law, as stated above, may be represented by the mathematical equation:

$$J \oint dQ = \oint dW \quad (2:1)$$

**2:2. The Closed-system Process.** Let a closed system be caused to follow any state path during a change from state 1 to state 2. The change in stored energy, now established as a property of the system, will be dependent only on the end states and may be designated as  $E_2 - E_1$ , or as  $\Delta E$ . But the change in  $E$  must have resulted from a net flow of energy across the system boundaries, and, for a closed system, this could have been only in the form of heat or work. The net amount of heat flow which accompanied the process is dependent not only upon the path but upon the way in which that path was followed. To represent it we shall use the notation  ${}_1Q_2$ , indicating that this heat flow took place as the system changed its state, depends on the manner in which the change of state was effected, and cannot be calculated on the basis of the end states alone. Similar reasoning may be applied to the net work that accompanied the process, and it will be designated as  ${}_1W_2$ . Then

Energy flow in—energy flow out = change in stored energy

or, taking into account the conventions that have been adopted as to the signs of heat and work,

$$J {}_1Q_2 - {}_1W_2 = J(E_2 - E_1) = J \Delta E \quad (2:2)$$

This is the general statement of the First Law as it applies to a closed-system process. In the absence of motion, gravity, capillarity, magnetism, and electricity, the foregoing equation becomes

$$J {}_1Q_2 - {}_1W_2 = J(U_2 - U_1) = J \Delta U \quad (2:3)$$

Occasionally the process that connects states 1 and 2 is so complicated that it is impossible to fit a single description to its entire length. In that case it may be divided into segments and described piece by piece. The change of stored energy over an infinitesimal segment may be expressed as  $dE$  (or  $dU$  in the case of the simple system) and the total of all these infinitesimal changes summed to measure the total change of stored

energy of the system during the entire process, or  $\int_1^2 dE = E_2 - E_1$ . The same general procedure can be followed in measuring  ${}_1Q_2$  and  ${}_1W_2$  except that the infinitesimal amount of heat and work, not being properties and therefore not dependent solely on the end states of the infinitesimal segments into which the process has been divided, cannot properly be expressed as exact derivatives. To indicate this difference and to keep ourselves reminded of it, we shall employ the symbols  $\partial Q$  and  $\partial W$  to represent their infinitesimal magnitudes. Then  ${}_1Q_2 = \int_1^2 \partial Q$ , and  ${}_1W_2 = \int_1^2 \partial W$ . For an infinitesimal process, Eqs. (2:2) and (2:3) become

$$J \partial Q - \partial W = J dE \quad (\text{general, closed system}) \quad (2:4)$$

$$J \partial Q - \partial W = J dU \quad (\text{simple closed system}) \quad (2:5)$$

Examination of Eqs. (2:2) to (2:5) indicates that, while heat and work considered individually are not properties of the closed system, their difference during any process through which the system is carried is a property of the system since it will depend only on the end states. Thus if by some means (as yet unknown to us) the maximum amount of work that can accompany the tracing of a given path with fixed end points can be established, the maximum amount of heat flow that can be associated with that path can be calculated when the change of stored energy of the system, as based on the end states, may be determined. As the work which accompanies the tracing of the given path decreases from this maximum, there must be a corresponding and equal reduction in the heat flow since the change in stored energy, being dependent only on the end states, will remain constant.

*Example 2:2A.* During a certain process a simple system receives 20 Btu of heat as its internal energy is increased by 30 Btu. What amount of work is involved in the process?

*Solution.* Applying Eq. (2:3),

$$(778)(+20) - {}_1W_2 = (778)(+30) \\ {}_1W_2 = -7780 \text{ ft-lb}$$

Justifying the signs used in substituting in the equation, it will be remembered that heat flow into the system is positive and that, if the internal energy increases,  $U_2 > U_1$ . Similarly, consistent with the sign convention that applies to work, it is evident that work was done *on* the system during the process.

*Example 2:2B.* The maximum amount of work that can accompany a certain path for a simple system is  $-10,000$  ft-lb. The change of internal energy of the system between the end states of that path is  $+20$  Btu. (a) What is the maximum heat flow that can take place during the traversal of the specified path? (b) If, owing to a change in the description of the method by which the given path was traversed, the amount of work was reduced to  $-20,000$  ft-lb, what heat flow would accompany this new process?



*Solution:*

(a) Applying Eq. 2:3,

$$\begin{aligned} 778({}_1Q_2)_{\max} - (-10,000) &= (778)(+20) \\ ({}_1Q_2)_{\max} &= +7.15 \text{ Btu (into the system)} \end{aligned}$$

(b) Note that the amount of work has decreased in the *algebraic* sense. Substituting in Eq. (2:3),

$$\begin{aligned} 778 {}_1Q_2 - (-20,000) &= (778)(+20) \\ {}_1Q_2 &= -5.7 \text{ Btu (out of the system)} \end{aligned}$$

Or, applying the principle that the heat flow must have decreased in exactly the amount of decrease of work,

$${}_1Q_2 = 7.15 - 10,000/778 = -5.7 \text{ Btu}$$

**2:3. Work and the Closed System.** In the absence of motion, gravity, capillarity, electricity and magnetism,<sup>1</sup> work may pass across the boundaries of the closed system in only two ways. One of these is the paddle-wheel method described in Art. 1:7. This process permits only the inward passage of work (negative work), and the process cannot be retraced (though the system may be returned to its original state over the same path). Paddle-wheel work is possible because of a property of the fluid called viscosity and takes place through the agency of friction. Intermolecular friction accompanies turbulence such as is caused by the paddle wheel. *Friction always has the effect of producing a change in the state of the system, when work is done on it, which could have been produced by a flow of heat.* But since work is a much more costly and valuable form of energy than heat, frictional processes are wasteful processes and to be avoided as far as possible. In general, in developing the theoretical principles which limit the performance of engineering apparatus, it will be our policy to base our calculations on an assumed absence of friction. Thus the performance of the actual machine, in the operation of which friction always is a factor, can approach but never reach the theoretical standards that apply.

The only other method by which work may pass across the boundaries of the closed system is by a change in the position of those boundaries due to an expansion or a contraction of the system. An increase in system volume would, in general, indicate positive work, a decrease would be accompanied by negative work. Typical of a transfer of energy in the form of work in this manner is work done on a piston.

<sup>1</sup> In analyzing thermodynamic processes of the closed system, energy storage due to the effects of motion, gravity, capillarity, magnetism, and electricity will hereafter be considered negligible unless otherwise specifically stated. Also, a simple system will be assumed so that all properties are established if the values of only two which are independent of each other are known.



**2:4. Maximum Work on a Piston.** Suppose the system to be confined within a cylinder which is fitted with a movable piston as illustrated in Fig. 2:1. The original position of the piston is shown in full lines and the corresponding pressure and volume of the system are  $P_1$  and  $V_1$ . As the system expands, overcoming the resistance offered by external systems such as the piston, piston rod, fly-wheel, and any external fluid system (as, for instance, the atmosphere, which may oppose the motion of the piston by exerting pressure against its outer surface), the variation of system pressure and volume is traced, resulting in the path 1-2 on the pressure-volume diagram. In practice, this graph may be made by means of an instrument called an *indicator*, which is connected, for the measurement of pressure, through one of the stationary walls that form a part of the system boundary and which is indirectly connected to the piston to give the lateral movement that measures the change in system volume.

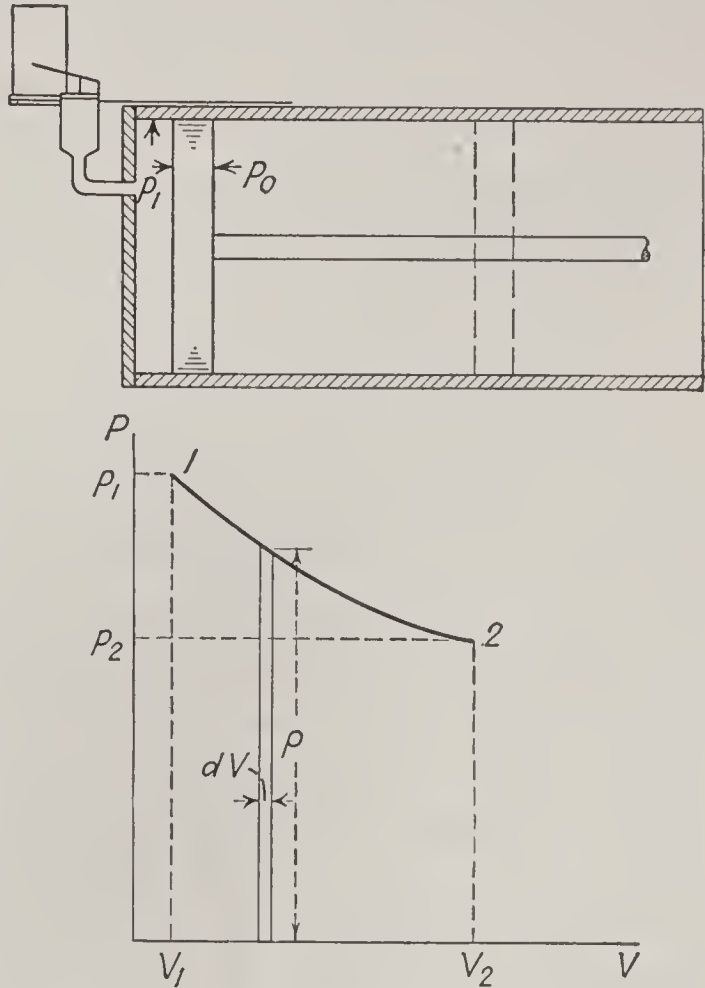


FIG. 2:1. Maximum work on a piston.

As an infinitesimal section of the path is traversed, the average pressure is  $P$ , and if the area of the face which the piston presents to the system (measured in a plane perpendicular to the direction of piston movement) is denoted by  $A$ , the average force on the piston is  $PA$ . During the infinitesimal change in volume that has taken place ( $dV$ ), the piston has moved a distance  $dV/A$  and the resultant work is  $(PA)(dV/A) = P dV$ ; this is represented by the segmental area shown in Fig. 2:1. For the entire process, the work which has left the system is the sum of these areas between states 1 and 2, or

$${}_1W_2 = \int_1^2 P dV \quad (2:6)$$

If an expression for  $P$  in terms of  $V$  that represents the relation between them along the path is available,  ${}_1W_2$  can be found by mathematical integration. Or, if more convenient, the area between the path and the  $V$  axis can be measured graphically or by any other means and  ${}_1W_2$  can be thereby evaluated. If  ${}_1W_2$  is to be measured in foot-pounds, that result can be obtained by expressing  $P$  in pounds per square foot absolute and  $V$

in cubic feet. Note that as far as the calculation of the work that left the system is concerned, it makes no difference whether the resistance which was overcome was offered by the piston and other parts of the mechanism or by the pressure of the atmosphere operating against the rear face of the piston; this explains why  $P$  is expressed in term of the *absolute* pressure.

In the development of Eq. (2:6) the pressure was explained as that operating against any stationary part of the boundary; it is only because gravity is neglected that a common pressure can be assigned to parts of that boundary at different elevations. During the expansion on which our development was based, the piston is moving outward, and the velocity with which the molecules of the system strike the inner face of the piston must be correspondingly less than their velocity relative to the stationary parts of the boundary. Based on the concept of pressure outlined in the first chapter, the pressure which the system exerts on the face of the piston must be less than that exerted against the stationary boundary and the work accompanying the process less than as calculated by Eq. (2:6). Considering the very much greater speed of the molecule as compared with piston speeds employed in usual engineering practice, this effect is small, but  ${}_1W_2$ , as calculated by Eq. (2:6), none the less measures the *maximum* work which can accompany the tracing of a given state path as the system expands; to develop it in the full amount requires that the motion of the piston shall be indefinitely slow. During a compression, the piston moves inward, and the pressure that the system applies to the inner face of the piston is greater than that against the stationary boundaries. The absolute amount of work involved is, in this case, larger than is represented by the area between the path and the  $V$  axis. However, this is negative work and, in the algebraic sense, smaller than  $\int_1^2 P dV$ . Thus the application of Eq. (2:6) gives the maximum amount of work, *in the algebraic sense*, that can accompany the tracing of the path. This is the maximum amount of work to which reference was made in Art. 2:2 and which, as it now develops, can be measured as  $\int_1^2 P dV$ .

*Example 2:4.* A closed system changes from an initial pressure of 50 psig and volume of 10 ft<sup>3</sup> to a final pressure of 70 psig and a final volume of 8 ft<sup>3</sup>. The path is represented by a straight line on a diagram for which the pressure and volume are the coordinates. (a) What maximum work could accompany any process during which this path was followed? (b) If the original internal energy was 150 Btu and the final 170 Btu, what maximum heat flow could have taken place?

*Solution:*

(a) To contrast the two methods by which the work area may be measured, both will be applied. Applying Eq. (2:6),

$$p_1 = 64.7 \text{ psia}; p_2 = 84.7 \text{ psia}; V_1 = 10 \text{ ft}^3; V_2 = 8 \text{ ft}^3$$



By the methods of analytical geometry, the equation of the straight line passing through these points on a  $pV$  graph is

$$p = 164.7 - 10V \text{ or } P = 144(164.7 - 10V)$$

$${}_1W_2 = 144 \int_{V_1}^{V_2} (164.7 - 10V)dV = 144 [164.7V - 5V^2]_{10}^8 = -21,500 \text{ ft-lb}$$

The work area is trapezoidal and is negative in sign since the process proceeds from right to left. The area is  $144 \left( \frac{64.7 + 84.7}{2} \right) (-2) = -21,500 \text{ ft-lb}$ .

(b) Maximum heat flow will accompany maximum work, and, applying Eq. (2:3),

$$778 {}_1Q_2 - (-21,500) = 778(170 - 150)$$

$${}_1Q_2 = -7.6 \text{ Btu}$$

This is the maximum heat flow in the algebraic sense.

**2:5. Useful Work.** The reader will have observed that in Fig. 2:1 the total work delivered by the system during the expansion process could not have been delivered to the more remote parts of the engine mechanism, even if all parts had been frictionless, because a portion was dedicated to the task of pushing back the atmosphere. This is a characteristic limitation that applies to the process as carried out in practice; the *surroundings* must be taken into consideration. In most cases the surroundings are represented by the atmosphere, which is conceived as a *medium* so vast in extent that a change in volume of the finite system produces no significant change in the pressure of the medium nor does a flow of heat to or from the finite system result in any change in the temperature of the medium. The temperature and pressure of the medium are therefore assumed to be constant and are designated as  $T_0$  and  $P_0$ . In the case of the expansion used as an example in Art. 2:4 the part of the total work that was absorbed by the atmosphere is  $P_0(V_2 - V_1)$ , and the maximum work which can be applied to useful purposes is  ${}_1W_2 - P_0(V_2 - V_1)$ . This is not of immediate importance to us, but reference will again be made to it at a later stage in our discussion. The distinction applies only to the process, for if a cycle is eventually traversed, the atmosphere will have contributed as much work during the return of the piston to its original position as it absorbed on the outward journey.

**2:6. Constant-volume Processes.** If a constant-volume path is followed, as in Fig. 2:2, the area under the state path, and thus the maximum work that can accompany any process which traces that path, is zero. As we have seen in Art. 1:7, the path 1-2 could have been traced by supplying work instead of heat to the system (the paddle-wheel process); this work would have been negative in sign with respect to the system and thus less than zero in the algebraic sense. Moreover, the reverse path

2-1 could not have been accompanied by the delivery of work by the system.

The maximum-work process is a *limiting* process; in applying Eq. (2:3) to a constant-volume path, no value greater than zero may be assigned to

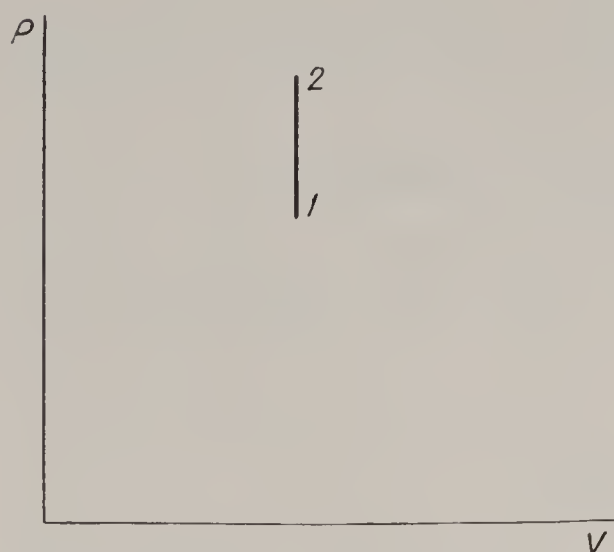


FIG. 2:2. The constant-volume path ( $\int P dV = 0$ ).

$_1W_2$  (or  $_2W_1$ ), as that notation applies in Fig. 2:2. On the other hand, no limit exists to the amount of paddle-wheel work which may accompany the tracing of the path in either direction, for heat flow outward may occur simultaneously with work flow inward and increase the total amount of negative work required without limit. In attacking the problem of establishing the standards for the best possible performance of heat-work devices, our calculations are therefore based upon the maximum-work process as repre-

senting the minimum wastage of the more costly form of energy.

**2:7. The specific heat at constant volume,  $c_v$ ,** is sometimes nonrigorously defined as the amount of heat required to increase the temperature of unit weight of the substance by 1 deg while the volume remains constant. As has been demonstrated in the preceding article, that effect may be accomplished without heat flow or even with negative heat flow. A more rigorous definition would specify that the limiting, or maximum-work, process was to be followed as the heat was supplied. Under these conditions,  $\partial W = 0$ , and Eq. (2:5) becomes  $\partial Q = du$ . Thus a rigorous definition of the specific heat at constant volume would express it as

$$c_v = \left( \frac{du}{dt} \right)_v \quad (2:7)$$

The specific heat at constant volume is of principal importance when the substance is in the gaseous phase; it is not ordinarily expressed for liquids or solids. Since it has a definite value corresponding to each state of the system, it is a property of the system.

*Example 2:7.* For the system and the process described in Example 1:10, calculate (a) the maximum work, (b) the maximum heat flow, and (c) the specific heat at constant volume,  $c_v$ .

*Solution:*

- (a) Since  $dV = 0$ , the maximum work is zero. [Eq. (2:6)]  
 (b) Based on Eq. (2:3), since  $(_1W_2)_{\max} = 0$ ,  $_1Q_2 = U_2 - U_1 = 30.6$  Btu. [Ex. 1:10]  
 (c)  $c_v = \left( \frac{\Delta u}{\Delta t} \right)_v = \frac{10.2}{120 - 60} = 0.17$  Btu/(lb)(°F) or Btu/(lb)(°R)



**2:8. Constant-pressure Processes.** The area under the constant-pressure path, illustrated in Fig. 2:3, is  $P(V_2 - V_1)$  or  $P_2V_2 - P_1V_1$ , and this is therefore the maximum work that may be developed. Substituting in Eq. (2:3),

$$J {}_1Q_2 - (P_2V_2 - P_1V_1) = J(U_2 - U_1)$$

$${}_1Q_2 = \left( U_2 + \frac{P_2V_2}{J} \right) - \left( U_1 + \frac{P_1V_1}{J} \right)$$

The quantity  $U + PV/J$  is evidently a composite property since it is expressed entirely in terms of properties. It is called *enthalpy* (en-thal'-py), and the symbol  $H$  will represent it. Since  $U$  and  $V$  are both extensive properties, enthalpy is also extensive; specific enthalpy, or enthalpy of unit weight, is denoted as  $h$ . Thus the following relations develop:

$$H = U + \frac{PV}{J} \quad h = u + \frac{Pv}{J} \quad (2:8)$$

$$({}_1Q_2)_{p, \text{ max work}} = H_2 - H_1 \quad (2:9)$$

An important warning must be inserted here. Although examination of Eqs. (2:8) and (2:9) indicate that enthalpy is conventionally measured in Btu and that changes of enthalpy can be used to measure heat flow, *under the special condition that a constant-pressure maximum-work process is followed*, the reader must not fall into the error of thinking of the enthalpy as a kind of stored energy of the system. As a property, its values may be tabulated for each state of the system, and it finds usefulness in ways such as may be inferred from Eq. (2:9); other uses of this property will develop later.

Figure 2:4 illustrates schematically the manner in which the constant-pressure process may be conceived as a maximum-work process. As heat enters, the gas system confined below the weighted, frictionless piston expands *slowly* against the constant pressure created by the weight of the piston plus the pressure of the atmosphere acting on its upper surface. The maximum amount of work is performed *by* the expanding gas system and equals  $P(V_2 - V_1)$ ; this is also the amount of work *received* by the external system that consists of the piston and the atmosphere.

In the course of the process which was described in the preceding paragraph, heat has been received from some external system which at all times has a temperature higher than that of the confined system. If,

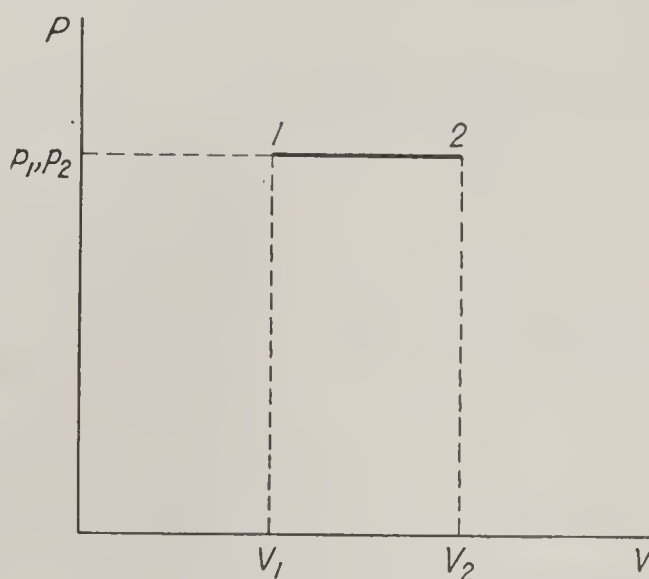


FIG. 2:3. The constant-pressure path [ $\int P dV = P(V_2 - V_1) = P_2V_2 - P_1V_1$ ].

after the confined system has completed its expansion to  $V_2$ , a cold body replaces the hot body from which heat was received during the original process, the direction of flow of heat will be reversed; the confined system

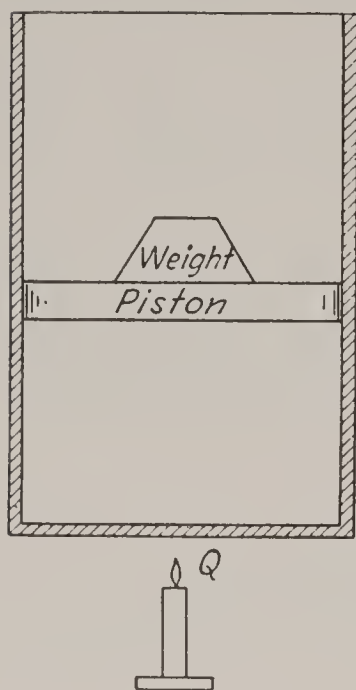


FIG. 2:4. The constant-pressure maximum-work process.

will again return, at constant pressure, to its original volume. As it does so, work is done on it by the piston and the atmosphere in the same amount that work was received by them during the expansion. Not only is the state path retraced but, as regards the enclosed gas system, the same is true of the process, for both the work and the net heat flow of the cycle are individually equal to zero. On the other hand, if all, or any part, of the energy *received* by the system during its expansion had been in the form of work, the system, though it could have returned to its original state over the same *state path*, could not have retraced the *process*; for the net work and net heat flow of the cycle would both be less than zero.

**2:9. The specific heat at constant pressure  $c_p$**  is the heat flow that will produce a temperature increase of one degree in one pound of the substance as a constant-pressure maximum-work process is carried out. Applying Eq. (2:9) in differential form to a unit weight of substance,

$$(\partial Q)_{p, \text{ max work}} = dh$$

$$c_p = \left( \frac{dh}{dt} \right)_p \quad (2:10)$$

The specific heat at constant pressure is a property that finds important uses in connection with all of the phases of the substance, solid, liquid, or gaseous.

*Example 2:9.* The system described in Example 1:10 traverses a path at a constant pressure of 50 psig in the course of which its temperature changes from 60 to 120°F. Calculate (a) the final volume of the system, (b) the maximum work that could accompany the process, (c) the maximum heat flow during the process, (d) the change of enthalpy of the system, (e) the specific heat at constant pressure for this substance. (f) Write an equation of state for this substance that will express the enthalpy in terms of the pressure and the volume.

*Solution:*

$$(a) \ v_2 = \frac{CT_2}{p_2} = \frac{0.37(120 + 460)}{50 + 14.7} = 3.31 \text{ ft}^3/\text{lb}; \ V_2 = 9.93 \text{ ft}^3$$

$$(b) \ ({}_1W_2)_{\text{max}} = P(V_2 - V_1) = (64.7)(144)(9.93 - 8.91) = 9500 \text{ ft-lb}$$

$$(c) \ u_2 = A + Bp_2v_2 = 16 + (0.46)(64.7)(3.31) = 114.7 \text{ Btu/lb}$$

$$u_2 - u_1 = 114.7 - 104.5 = 10.2 \text{ Btu/lb}; \ U_2 - U_1 = (3)(10.2) = 30.6 \text{ Btu}$$



From Eq. 2:3,

$$({}_1Q_2)_{\max} = U_2 - U_1 + ({}_1W_2)_{\max}/J = 30.6 + \frac{950.0}{778} = 42.8 \text{ Btu}$$

(d) From Eq. (2:9),  $H_2 - H_1 = ({}_1Q_2)_{p, \max} = 42.8 \text{ Btu}$ .

$$(e) \ c_p = \left( \frac{\Delta h}{\Delta t} \right)_p = \frac{42.8}{3(120 - 60)} = 0.238 \text{ Btu/(lb)(}^\circ\text{F)}$$

$$(f) \ h = u + Pv/J = A + Bpv + Pv/J = 16 + 0.46pv + 144pv/778 = 16 + 0.645pv$$

**2:10. The Constant-temperature (Isothermal) Process.** The system can be caused to remain at constant temperature if the cylinder in which it is confined is immersed in a constant-temperature bath and if the cylinder walls are perfect conductors of heat; *i.e.*, only an infinitesimal difference in temperature between system and bath is necessary to cause heat flow at any desired rate. The path traversed during a constant-temperature process may be illustrated as in Fig. 2:5, but it will be observed that this method of plotting does not lend itself to the direct calculation of  $\int P \, dV$  and thus enable the calculation of the maximum work that can accompany the performance of the path. However, for a simple system, all properties are established if any two that are independent of each other are known and to each point along the  $TV$  path a definite pressure is therefore attached. Assuming that an equation of state such as Eq. (1:6), connecting the temperature, pressure, and volume of the substance of which the system is composed, is available, these pressures can be determined and an equivalent  $PV$  path laid out. From this path the maximum work may be calculated. The change of internal energy is dependent only on the initial and final states and may be determined when a suitable equation of state [as Eq. (1:7), for example] is known to apply to the substance. Substitution in Eq. (2:3) will then make possible the calculation of the maximum heat flow that can accompany the process. The introduction of paddle-wheel work into the process will not change  $\Delta U$  if the end states are the same as for the maximum-work process but will reduce the work and the heat flow by amounts corresponding to the amount of such paddle-wheel work.

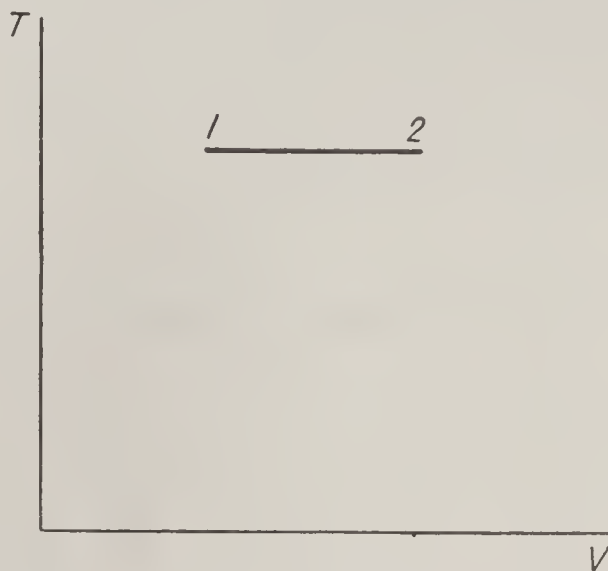


FIG. 2:5. The constant-temperature path.

*Example 2:10.* Assume a system composed of 2 lb of a substance for which the equations of state are represented by Eqs. (1:6) and (1:7). Let it expand at a constant temperature of  $50^\circ\text{F}$  (isothermally) from an initial pressure of 100 psia and volume of  $4 \text{ ft}^3$  to a final volume of  $8 \text{ ft}^3$ . Determine (a) the equation of the path in terms of  $p$  and  $v$ , (b) the final pressure of the system, (c) the change of internal energy

that takes place, and (d) the maximum work and maximum heat flow which can accompany the process.

*Solution:*

(a) For the purpose of substituting in Eq. (1:6),  $p_1 = 100$ ;  $v_1 = \frac{4}{2} = 2$ ;  $T_1 = 50 + 460 = 510$

$$C = pv/T = (100)(2)/510 = 0.393$$

The equation of the path is  $pv = 200$  or  $pV = 400$  and  $PV = (144)(400) = 57,600$ .

(b) Since  $p_1v_1 = p_2v_2$ ,  $p_2 = p_1v_1/v_2 = (100)(2)/4 = 50$  psia.

(c) Applying Eq. (1:7),  $u_1 = A + B(p_1v_1)$ , and  $u_2 = A + B(p_2v_2)$ . But, for this substance,  $p_1v_1 = p_2v_2$  during an isothermal, and  $\Delta u$  is therefore zero. [The reader is warned that this result is obtained only because of the special form of Eqs. (1:6) and (1:7) and it will not generally follow that an isothermal path is also one which is traced through states having the same internal energy.]

(d)  $({}_1W_2)_{\max} = \int_{V_1}^{V_2} P dV = 57,600 \int_{V_1}^{V_2} dV/V = 57,600 \log_e \frac{8}{4} = 39,900 \text{ ft-lb}$  and, applying Eq. (2:3),

$$({}_1Q_2)_{\max} = U + ({}_1W_2)_{\max}/J = 0 + 39,900/778 = 51.3 \text{ Btu}$$

**2:11. Constant-internal-energy Processes.** The closed system can traverse a constant-internal-energy path only by maintaining an exact balance in the rate at which heat and work cross its boundaries; *i.e.*, the rate of heat flow, if inward, must be exactly equal to the rate at which work is delivered by the system to other systems. Thus, applying Eq. (2:3),  $J {}_1Q_2 = {}_1W_2$ . The path may be illustrated as in Fig. 2:6.

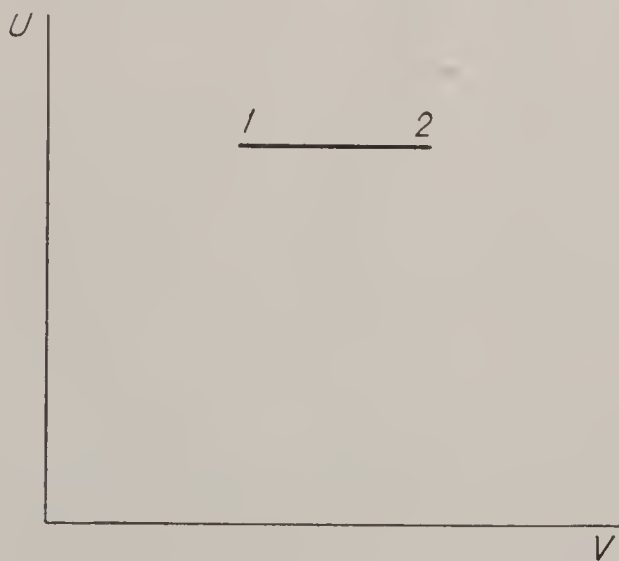


FIG. 2:6. The constant-internal-energy path.

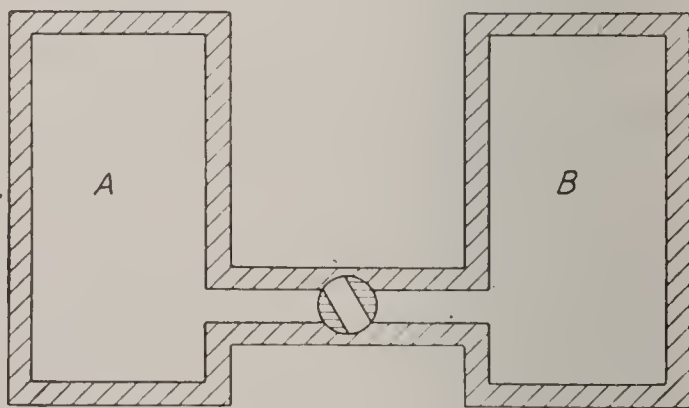


FIG. 2:7. The zero-work constant-internal-energy process.

The calculation of the amount of work that can accompany the tracing of the constant-internal-energy path requires that the path shown in Fig. 2:6 be transferred to pressure-volume coordinates. This can be done if an equation of state such as Eq. (1:7) is available;  $\int P dV$  can then be evaluated. The maximum heat flow will be equal to the maximum work when expressed in terms of the same energy unit.



A special type of constant-internal-energy process is of interest. Suppose the system originally to be confined in a section of a container with rigid nonconducting walls. This vessel is designated as *A* in Fig. 2:7 and is connected with a vessel *B*, also with rigid nonconducting walls, through an insulated passage that includes a closed valve. Originally, vessel *B* has been voided of all matter. The valve is now opened, and the molecules of the system will rush in to occupy this voided space until the pressure in the two vessels is equalized. The resistance of no external system has been overcome, and thus the amount of work involved is zero. The reader may find it helpful to conceive of work as done on an imaginary piston which is moving with the speed of the molecules themselves and therefore offers no resistance to the expansion of the system. Since the passage of heat was prevented by the nonconducting walls of both vessels, the internal energy, according to Eq. (2:3), must have remained constant. For this special case, not only  $\Delta U$  but also  ${}_1Q_2$  and  ${}_1W_2$  are zero; yet the *state* of the system has changed.

The path followed during this process would have been difficult to trace, but points along that path could be located by allowing the total expansion to take place by stages. That is, a series of partitions could be provided in the voided chamber, and the expansion of the system could be halted at each successive partition long enough to allow an equilibrium state to be reached. The pressure and the volume could then be measured and a point on the pressure-volume graph plotted. A path drawn through these points would agree exactly with that followed during a maximum-work process, but, of course, the area under it would not have the same significance.

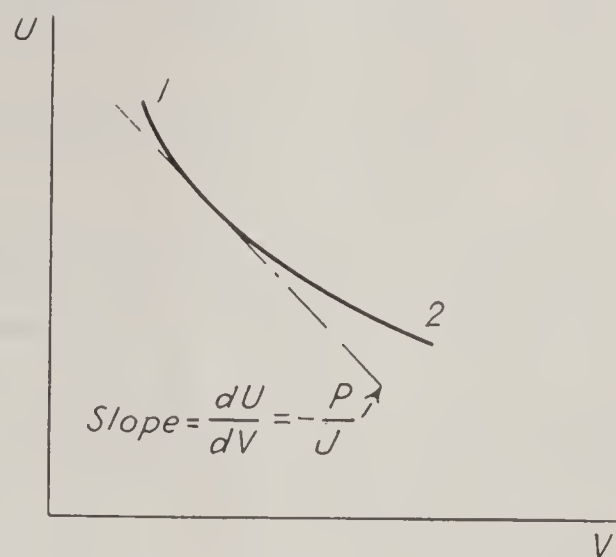


FIG. 2:8. The maximum-work adiabatic process.

**2:12. The Adiabatic Process.** By definition, the adiabatic process involves no heat flow. Thus, from Eq. (2:5),  $dU = -\partial W/J$ . If this is a maximum-work process,  $P dV$  may be substituted for  $\partial W$ , and it follows that

$$J dU = -P dV$$

or

$$\frac{dU}{dV} = -\frac{P}{J} \quad (2:11)$$

Thus, for the maximum-work adiabatic process, the path will have the form shown in Fig. 2:8, the slope at any point being negative and proportional to the pressure. Assuming that a suitable equation of state is

available, a corresponding path may be traced on a graph having pressure-volume coordinates, and the maximum work that may accompany the process can be determined.

When an algebraic equation of state such as Eq. (1:7) is available,  $du/dv$  may be determined from it as it applies to *any* process and, for the special case of the maximum-work adiabatic, placed equal to  $-P/J$ . From this equality the equation relating pressure and volume during a maximum-work adiabatic may be obtained.

*Example 2:12A.* Using Eq. (1:7), derive the equation that applies to the maximum-work adiabatic process when the system is composed of an ideal gas.

*Solution:*

$$u = A + Bpv \quad [\text{Eq. (1:7)}]$$

$$du = Bp dv + Bv dp \text{ (any process)}$$

$$\frac{du}{dv} = B \left( p + v \frac{dp}{dv} \right) = -\frac{P}{J} \text{ (maximum-work adiabatic process)} \quad [\text{Eq. (2:11)}]$$

or

$$B \left( p + v \frac{dp}{dv} \right) = -\frac{144}{778} p = 0.185p$$

and, dividing by  $p$ ,

$$B \left( 1 + \frac{v}{p} \frac{dp}{dv} \right) = -0.185$$

from which

$$\frac{B + 0.185}{B} = -\frac{v}{p} \frac{dp}{dv}$$

Dividing by  $pv$  and transposing,

$$\frac{dp}{p} + \frac{B + 0.185}{B} \frac{dv}{v} = 0$$

Integrating,

$$\log_e p + \frac{B + 0.185}{B} \log_e v = \text{const}$$

or

$$pv^k = \text{const} \quad (2:12)$$

when

$$k = \frac{B + 0.185}{B} \quad (2:13)$$

The path shown in Fig. 2:8 applies to the maximum-work adiabatic only. The process which it represents may be traversed in either direction. During the expansion 1-2, work is done by the system at the expense of its internal energy; during the compression 2-1, the increase of internal energy exactly equals the work supplied by external systems.

*Example 2:12B.* The system described in Example 1:10 has an initial pressure of 50 psig and an initial temperature of 60°F as in that example. As the result of a



maximum-work adiabatic process, its pressure decreases to atmospheric pressure. Calculate (a) the final volume of the system, (b) its final temperature, (c) the work that accompanies the process, (d) the change of internal energy of the system as a result of the process.

*Solution:*

(a) From Eq. (2:12),  $k = (0.46 + 0.185)/0.46 = 1.4$ .

$$p_1 v_1^{1.4} = p_2 v_2^{1.4} \text{ or } v_2 = v_1 \left( \frac{p_1}{p_2} \right)^{1/1.4} = 2.97 \left( \frac{64.7}{14.7} \right)^{0.713} = (2.97)(2.88) = 8.55 \text{ ft}^3/\text{lb}$$

$$V_2 = (3)(8.55) = 25.65 \text{ ft}^3$$

(b)  $T_2 = p_2 v_2 / C = (14.7)(8.55) / 0.37 = 339^\circ\text{R}$  or  $-121^\circ\text{F}$

(c) The process takes place at maximum work, and therefore  ${}_1W_2 = \int_{V_1}^{V_2} P dV$ .

$$pv^k = \text{const} = p_1 v_1^k = (64.7)(2.97)^{1.4} = (64.7)(4.6) = 297$$

$$P = 144p = \frac{(144)(297)}{v^{1.4}} = \frac{42,700}{v^{1.4}}; dV = 3 dv$$

$$\begin{aligned} {}_1W_2 &= \int_{V_1}^{V_2} P dV = (42,700)(3) \int_{v_1}^{v_2} \frac{dv}{v^{1.4}} = 128,100 \int_{2.97}^{8.55} \frac{dv}{v^{1.4}} \\ &= (128,100)(-2.5) \left( \frac{1}{8.55^{0.4}} - \frac{1}{2.97^{0.4}} \right) \\ &= 71,700 \text{ ft-lb} = 92 \text{ Btu} \end{aligned}$$

(d)  $U_2 - U_1 = 3(u_2 - u_1) = 3B(p_2 v_2 - p_1 v_1) = (3)(0.46)[(14.7)(8.55) - (64.7)(2.97)]$   
 $= -92 \text{ Btu}$

If the work accompanying an adiabatic is less than the maximum, a multitude of paths may be traced by the system but these paths will not be retraceable as adiabatic processes. For example, a system may be increased in temperature at constant volume adiabatically if the paddle-wheel process is used to supply the necessary energy; the reader's own experience can hardly fail to tell him that, although the path may be retraced, it cannot be retraced as an adiabatic. Another example is the unrestrained and adiabatic expansion at constant internal energy described in Art. 2:11; after the system has expanded to occupy the full volume of both vessels, it cannot be restored to its original pressure and volume at constant internal energy by any process which does not involve work and heat flow.

**2:13. The Paddle-wheel Process and Friction.** The paddle-wheel process has been used in preceding pages to illustrate one of the two reasons why the work with respect to a system as a given state path is traced may be less than the maximum; the other was found in the difference in the pressure that the system exerted against its moving and its stationary boundaries as during an expansion which was wholly or partially unrestrained.

The paddle-wheel process as described heretofore was a calculated process in which the effects of intermolecular friction were deliberately invited to accomplish a certain effect. That effect was to bring about a change in the state of the system, by supplying work to it, which might

have been produced by heat flow alone. Since this has been condemned as wasteful (energy being more valuable in the form of work than as heat), some confusion may be caused in the mind of the reader as to why the paddle-wheel process was ever contemplated. The explanation is that the paddle-wheel process simply exemplifies the effects of friction wherever and however it may develop. Friction is always present in practical apparatus in some degree although it may be reduced toward zero *as a limit* as, for instance, by improved methods of lubrication.

As the piston of Fig. 2:1 moves, during either an expansion or a compression of the system, some friction will develop between it and the cylinder walls. The effect of that friction is the same as that of a paddle wheel since it reduces the net work of the process (in the algebraic sense) regardless of the direction of piston movement and because the equivalent amount of energy is changed to the form of heat. This is a wasteful process, as we have observed, but at least it has the virtue of being unavoidable rather than deliberate. The paddle-wheel process thus represents the effects of friction as they bring about deductions from the maximum work that can accompany a given path, and we may revise an earlier statement to the form: *Friction and unrestrained expansion will account for a reduction in the work that accompanies the tracing of a given path from the maximum, or  $\int P dV$ .*

**2:14. The Closed-system Cycle.** The *power plant* has the function of delivering work *continuously*. Power is the word that is used to describe

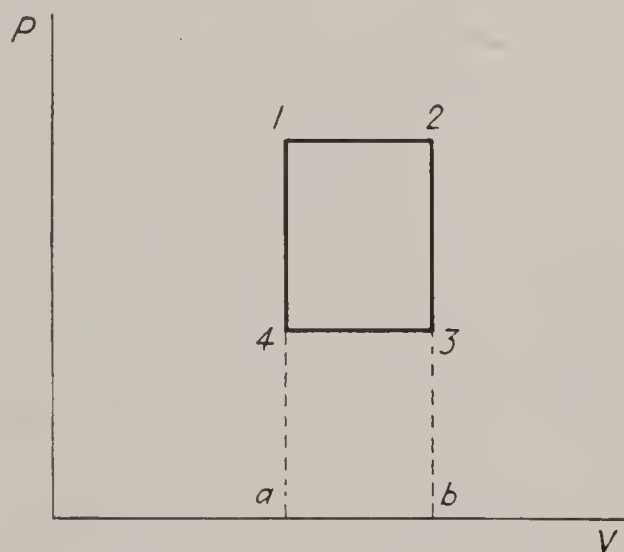


FIG. 2:9. A closed-system cycle.

the rate at which work is delivered by such devices. An important power unit is the horsepower, which is arbitrarily defined as a rate of work delivery equivalent to the delivery of 550 ft-lb each second. The kilowatt, equivalent to 1.34 hp, is also frequently used. The horsepower hour is the total amount of energy represented by the delivery of work at the rate of 550 ft-lb/sec (1 hp) over a time period of 1 hr, or 3600 sec. A similar unit, 1.34 times as large, is the kilo-

watthour; this is the unit in terms of which energy is usually bought and sold. It will be noted that it is *energy* that is purchased although the rate at which that energy is accepted by the consumer is often a factor in establishing the unit price per kilowatthour.

In order to deliver work *continuously*, the power plant operates on some sort of cycle, returning the system periodically to its original state. One closed-system cycle is illustrated in Fig. 2:9, the cycle being composed of



two constant-pressure and two constant-volume paths. Assuming that the processes are carried out with maximum work, which would be possible in the actual power plant only as a limiting condition, the rate of work delivery per cycle is represented by the area enclosed within the cycle, for the (positive) work during the constant-pressure expansion 1-2 is the area  $a-1-2-b$  and the (negative) work accompanying the constant-pressure compression 3-4 is area  $b-3-4-a$ ; no work enters into the constant-volume processes 4-1 and 2-3.

From the First Law, the area enclosed within the cycle also represents the net heat flow (*heat flow in* minus *heat flow out*) during the cycle. When the processes that comprise the cycle of Fig. 2:9 are analyzed on the basis of the First Law (and as maximum-work processes), it will be found that heat entered the closed system during processes 4-1 and 1-2 and left the system during processes 2-3 and 3-4. This implies that a change in the surroundings took place in the course of the cycle, for the temperature of those surroundings must have been higher than the temperature of the system during processes 4-1 and 1-2, to account for the entry of heat, and lower than the temperature of the system during processes 2-3 and 3-4, as heat left the system. It may be shown that the highest temperature reached by the system in the course of the cycle is at point 2. If an external reservoir is available from which heat may be withdrawn at or above this temperature it will be capable of supplying the heat necessary to carry out processes 4-1 and 1-2; to this external reservoir is given the name of the *source*. Similarly, the lowest temperature reached by the system during the cycle is that corresponding to point 4, and the heat that leaves the system during processes 2-3 and 3-4 could be transferred to a reservoir at or below this temperature; this reservoir is termed the sink, or *refrigerator*. It will later be shown that at least one source and one refrigerator, which must differ in temperature, are required for *any* power cycle. It will follow that during any such cycle there must be a two-way flow of heat; that, during a certain process or processes of the cycle, heat must be accepted from the source and, during another part of the cycle, heat must be rejected to the refrigerator. Further, since for the power cycle the net flow of heat must be positive, the heat received from the source must exceed that rejected to the refrigerator.

**2:15. The heat engine** is defined as a device that has as its purpose the continuous production of work from heat and across the boundaries of which only heat and work may pass. In Fig. 2:10 the apparatus required for a heat engine that operates on a closed-system cycle is illustrated. The cylinder walls are nonconducting, but the head permits the passage of heat. A nonconducting cap is provided for the head so that heat flow can be entirely cut off if one or more of the processes traversed in the

course of the cycle is an adiabatic. Provision is made for rapidly shifting the source  $S$  into place at the head of the cylinder when the cycle requires that heat enter the system. Similarly, the refrigerator  $R$  is placed in that

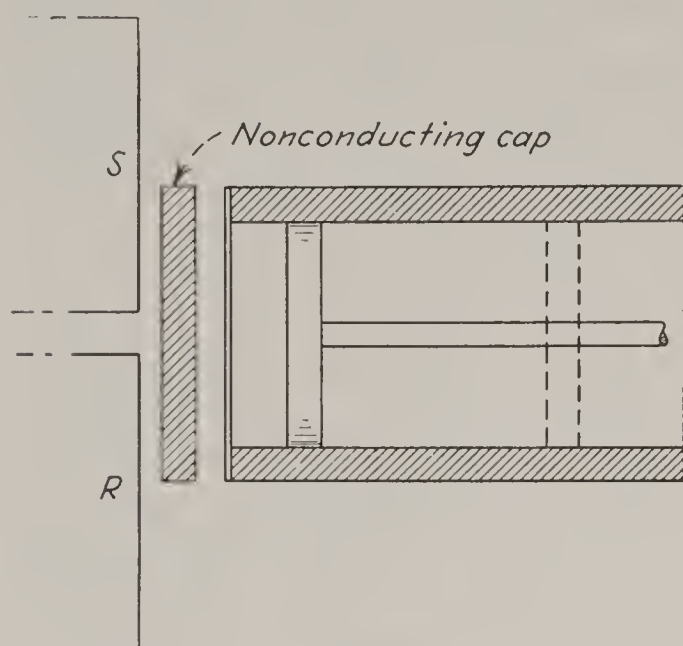


FIG. 2:10. The closed-system heat engine.

position when heat is to be removed. The limits of piston motion are as shown by the full and the dashed lines of the sketch.

It is evident that, while the closed-system cycle fulfills the technical requirements for a heat engine, it has serious practical limitations since the chamber in which work is performed must also act as a heat exchanger. Only a few actual engines are based on the closed-system cycle, and they are of small importance from the standpoint of practical performance.

However, from the speculative standpoint, we may profit greatly from a study of the limits of performance set by theory for the operation of this type of heat engine.

**2:16. Efficiency of a Heat Engine.** The performance of heat engines is compared in terms of their efficiencies. The efficiency  $\eta$  of a heat engine is defined as the rate at which it delivers work divided by the rate at which it receives heat from the source, or

$$\eta = \frac{W}{JQ_s} \quad (2:14)$$

in which  $W$  is the rate of work delivery, in foot-pounds per cycle or per unit of time, and  $Q_s$  is the rate at which heat is supplied the engine from the source, in Btu per cycle or per unit of time.

Since, by the First Law,  $J \oint \partial Q = \oint \partial W$  for any cycle, the work of the cycle is the difference between the rate of heat supply from the source,  $JQ_s$ , and the rate of heat rejection to the refrigerator,  $JQ_R$ , and an alternate expression for the efficiency is

$$\eta = \frac{Q_s - Q_R}{Q_s} \quad (2:15)$$

Either Eq. (2:14) or Eq. (2:15) may be used to calculate the efficiency of any heat engine according to the relative convenience of their application to that purpose.

*Example 2:16.* A heat engine causes the system described in Example 1:10 to traverse clockwise a cycle similar to that illustrated in Fig. 2:9. The engine makes



200 rpm, and  $V_1 = V_4 = 37 \text{ ft}^3$ ,  $V_2 = V_3 = 60 \text{ ft}^3$ ,  $p_1 = p_2 = 30 \text{ psia}$ ,  $p_3 = p_4 = 15 \text{ psia}$ . Assume all processes to be maximum-work processes, and calculate (a) the net work of the cycle, (b) the horsepower output of the engine, (c) the temperatures at points 1, 2, 3, and 4 around the cycle, (d) the heat supplied per cycle,  $Q_S$ , (e) the rate of heat rejection per cycle,  $Q_R$ , (f) the efficiency of the cycle.

*Solution:*

(a)  ${}_4W_1 = {}_2W_3 = 0$  (maximum-work constant-volume processes)

$${}_1W_2 = P_1(V_2 - V_1) = (30)(144)(60 - 37) = 99,400 \text{ ft-lb}$$

$${}_3W_4 = P_3(V_4 - V_3) = (15)(144)(37 - 60) = -49,700 \text{ ft-lb}$$

$$\begin{array}{l} \text{Net work of cycle} \\ (49,700)(200) \\ \hline (550)(60) \end{array} = 30.1 \text{ hp}$$

$$(b) \frac{(49,700)(200)}{(550)(60)} = 30.1 \text{ hp}$$

$$(c) T_1 = \frac{(30)(37)}{(0.37)(3)} = 1000^\circ\text{R, or } 540^\circ\text{F}$$

$$T_2 = \frac{(30)(60)}{(0.37)(3)} = 1620^\circ\text{R, or } 1160^\circ\text{F}$$

$$T_3 = \frac{(15)(60)}{(0.37)(3)} = 810^\circ\text{R, or } 350^\circ\text{F}$$

$$T_4 = \frac{(15)(37)}{(0.37)(3)} = 500^\circ\text{R, or } 40^\circ\text{F}$$

$$(d) Q_S = {}_4Q_1 + {}_1Q_2 = U_1 - U_4 + H_2 - H_1 = Mc_v(T_1 - T_4) + Mc_p(T_2 - T_1)$$

$$= (3)(0.17)(1000 - 500) + (3)(0.238)(1620 - 1000) = 698 \text{ Btu}$$

$$(e) -Q_R = {}_2Q_3 + {}_3Q_4 = U_3 - U_2 + H_4 - H_3 = Mc_v(T_3 - T_2) + Mc_p(T_4 - T_3)$$

$$= (3)(0.17)(810 - 1620) + (3)(0.238)(500 - 810) = -634 \text{ Btu}$$

$$Q_R = 634 \text{ Btu}$$

$Q_R$  might also have been found as the difference between  $Q_S$  and the net work of the cycle, or  $Q_R = 698 - 64 = 634 \text{ Btu}$ .

$$(f) \text{ Efficiency of the cycle} = \frac{Q_S - Q_R}{Q_S} = \frac{698 - 634}{698} = 0.0917, \text{ or } 9.17 \text{ per cent.}$$

### Problems

1. Referring to Prob. 9, Chap. 1, parts *a*, *b*, *c*, *e*, *f*, *i*, *j*, and *k*, does  $E$  increase, decrease, or remain constant in each case?

2. Figure 1:2 describes a state path graphically. Which of the following are sufficient to convert it to a description of the closed-system *process* as well? (a) The heat flow  ${}_1Q_2$  is known. (b) The work  ${}_1W_2$  is known. (c) Both  ${}_1Q_2$  and  ${}_1W_2$  are known. (d) Neither is known.

3. At the beginning of a process, the volume of a closed system is  $10 \text{ ft}^3$ , and the pressure is  $200 \text{ psia}$ . At the end,  $V_2 = 15 \text{ ft}^3$ ,  $p_2 = 200 \text{ psia}$ . The net work that accompanies the process is  $+100,000 \text{ ft-lb}$ . Calculate the heat flow during the process if the system consists of (a)  $16 \text{ lb}$  of gas  $W$ ; (b)  $7 \text{ lb}$  of gas  $X$ ; (c)  $11 \text{ lb}$  of gas  $Y$ ; (d)  $1.5 \text{ lb}$  of gas  $Z$ .

4. During a certain process,  $150,000 \text{ ft-lb}$  of work enters a closed gas system, and  $50 \text{ Btu}$  of heat leaves it. What change takes place in the temperature of the system and in its internal energy if the system consists of (a)  $10 \text{ lb}$  of gas  $W$ ; (b)  $4 \text{ lb}$  of gas  $X$ ; (c)  $8 \text{ lb}$  of gas  $Y$ ; (d)  $2 \text{ lb}$  of gas  $Z$ ?

5. A closed system traverses a cycle which is composed of four processes. The first process is an expansion during which  $100 \text{ Btu}$  of heat enters the system and  $25,000 \text{ ft-lb}$  of work leaves the system; the second process, also an expansion, is accompanied

by no heat flow while 30,000 ft-lb of work leaves the system; the third, a compression, sees heat leaving the system in the amount of 80 Btu while 35,000 ft-lb of work enters across the boundary; the fourth process is adiabatic. What amount of work accompanies the fourth process?

6. The temperature of a 1-lb closed system increases by  $150^{\circ}\text{F}$  during a process which is accompanied by an outward heat flow of 35 Btu. Calculate the work of the process if the system consists of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

7. The temperature of a closed gas system weighing 2 lb decreases by  $100^{\circ}\text{F}$  during a process. What is the difference between the heat flow and the work of the process if the system consists of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ ?

8. In Prob. 7, if the process takes place at constant volume, what maximum heat flow may accompany it in each case?

9. A closed container with rigid nonconducting walls contains a system consisting of a gas and an *electrical heating element*. Current is supplied the latter from a source outside the container; as a result, the temperature and pressure of the gas rise. Is the work of the process a maximum? Is the heat flow a maximum? Is the equivalent of paddle-wheel work performed? If so, what special kind of friction is involved? How does the system differ from that of Art. 2:3?

10. A closed system expands at a constant pressure of 120 psia from an initial volume of  $1.0\text{ ft}^3$  to a final volume of  $1.4\text{ ft}^3$ . What maximum work could accompany the process? If the system is returned to its original state over the same state path, what is the maximum work for the second process? What is the maximum work of the cycle formed by the two processes?

11. At a constant pressure of 1 atm, the volume of a closed system changes from 20 to  $17\text{ ft}^3$ . What maximum work may accompany the process?

12. A closed system changes from an initial pressure of  $p_1 = 40\text{ psia}$  and volume  $V_1 = 5\text{ ft}^3$  to a final pressure  $p_2 = 20\text{ psia}$  and volume  $V_2 = 10\text{ ft}^3$  over a state path which is a straight line on  $pV$  coordinates. What maximum amount of work may accompany the process?

13. The end states are the same as in Prob. 12, but the path is hyperbolic with  $pV = \text{const}$ . Calculate the maximum work.

14. The initial and final states of an expanding closed system are as in Prob. 10, but the path is a circular arc, convex upward and having its center at  $p_c = 120\text{ psia}$ ,  $V_c = 1.2\text{ ft}^3$ . What maximum work may accompany the process? If the system is returned to its initial state over a circular arc having the same center but concave upward, what maximum work may accompany this second process? What maximum work may accompany a cycle formed of the two processes?

15. If the expansion of Prob. 14 takes place in a cylinder fitted with a piston which is backed by the pressure of the atmosphere (14.7 psia), what maximum useful work could accompany the expansion? On the return process, what is the maximum useful work? What is the maximum useful work of the cycle? Compare with the work of the cycle as calculated in Prob. 14.

16. A part of the resistance offered by the piston to the expansion of the system of Prob. 10 is due to the pressure of the atmosphere (14.7 psia) on its back face. What maximum useful work could accompany the expansion? What maximum useful work could accompany the return process? What is the maximum useful work of the cycle? Compare with the work of the cycle as calculated in Prob. 10.

17. During a process that takes place at constant volume, the temperature of a closed system increases by  $100^{\circ}\text{F}$ . What maximum heat flow may accompany the process if the system consists of (a) 5 lb of gas  $W$ ; (b) 3 lb of gas  $X$ ; (c) 4 lb of gas  $Y$ ; (d) 1 lb of gas  $Z$ ?



18. Calculate the specific heat at constant volume,  $c_v$ , of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ .

19. If  $\left(\frac{\partial Q}{\partial t}\right)_v$  represents the rate at which heat flows across the boundaries of a 1-lb closed system during a constant-volume process, which of the following relations are not possible? (a)  $\left(\frac{\partial Q}{\partial t}\right)_v > c_v$ ; (b)  $\left(\frac{\partial Q}{\partial t}\right)_v < c_v$ ; (c)  $\left(\frac{\partial Q}{\partial t}\right)_v = c_v$ ; (d)  $\left(\frac{\partial Q}{\partial t}\right)_v < 0$ .

20. During a process that takes place at constant pressure, the temperature of a closed system increases by  $100^\circ\text{F}$ . What maximum heat flow may accompany the process if the system consists of (a) 5 lb of gas  $W$ ; (b) 3 lb of gas  $X$ ; (c) 4 lb of gas  $Y$ ; (d) 1 lb of gas  $Z$ ?

21. Write an equation that will express the specific enthalpy as a function of the pressure and the specific volume for (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ . Calculate the specific heat at constant pressure for each of these gases.

22. A closed gas system changes from  $p_1 = 150$  psia,  $V_1 = 2$  ft<sup>3</sup>, to  $p_2 = 100$  psia,  $V_2 = 1$  ft<sup>3</sup>. Calculate the change of enthalpy of the system if it is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

23. The isothermal expansion of a closed gas system starts from  $p_1 = 200$  psia,  $V_1 = 1$  ft<sup>3</sup>, and ends when the volume becomes 10 ft<sup>3</sup>. What are the maximum work of the process, the maximum heat flow, and the change of internal energy of the system, if it is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ ?

24. A closed gas system is compressed isothermally at  $200^\circ\text{F}$  from  $p_1 = 15$  psia to  $p_2 = 75$  psia. Calculate the maximum work and the maximum heat flow of the process and the change of enthalpy of the system if the system is composed of 1 lb of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

25. Show that the maximum work of an isothermal process is given by

$${}_1W_2 = 144MCT \log_e \frac{p_1}{p_2}$$

if the system is composed of an ideal gas.

26. A simple closed system which is *not* composed of an ideal gas undergoes an isothermal process. Which of the following statements are *necessarily* true? (a)  $J_1Q_2 = {}_1W_2$ ; (b)  $\Delta U = 0$ ; (c)  $T_2 = T_1$ ; (d)  $p_1V_1 = p_2V_2$ .

27. A simple closed system *not* composed of an ideal gas goes through a process during which its internal energy remains constant. Which of the following statements are *necessarily* true? (a)  $J_1Q_2 = {}_1W_2$ ; (b)  $U_2 = U_1$ ; (c)  $T_2 = T_1$ ; (d)  $p_1V_1 = p_2V_2$ .

28. Does Eq. (2:11) apply to a closed system which is *not* composed of an ideal gas? Is it necessary that it be a simple system? Is the storage of energy due to motion, gravity, capillarity, magnetism, or electricity prohibited when this equation is to be applied? What changes, if any, would you suggest if it is to apply to (a) fluids in general; (b) complex systems; (c) systems which may store energy due to motion, etc.?

29. What is the value of the exponent  $k$  in the maximum-work adiabatic process if the closed system is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ ?

30. Show that, for an ideal gas, the maximum work that may accompany a closed-system adiabatic process may be expressed as

$${}_1W_2 = \frac{144(p_1V_1 - p_2V_2)}{k - 1} = \frac{144MC(T_1 - T_2)}{k - 1}$$

31. A closed gas system has an initial pressure of 100 psia, and an initial volume of 1 ft<sup>3</sup>. It undergoes a maximum-work adiabatic process, reaching a pressure of 20 psia.

Calculate the final volume, the work of the process, and the change of internal energy of the system if composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

32. A closed system goes through an adiabatic process. Which of the following statements is *necessarily* true? (a)  ${}_1W_2 = J(U_1 - U_2)$ ; (b)  $pV^k = \text{const}$ ; (c)  ${}_1Q_2 = 0$ . Explain your answers.

33. A simple closed system expands adiabatically and at constant atmospheric pressure. The initial volume is 7 ft<sup>3</sup>, the final 10 ft<sup>3</sup>. Calculate the work of the process and the change of internal energy if the system is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

34. A simple closed gas system undergoes an adiabatic process during which a constant-volume state path is followed. During the process the temperature increases by 100°F. Calculate the work of the process if the system weighs 1 lb and is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

35. For an ideal gas, express the ratio of the final to the initial absolute temperature,  $T_2/T_1$ , as the result of a maximum-work adiabatic process as (a) a function of the pressure ratio,  $p_2/p_1$ ; (b) a function of the volume ratio,  $V_2/V_1$ .

36. Prove that for an ideal gas the value of  $k$  equals the ratio  $c_p/c_v$ .

37. What is the energy equivalent, in Btu, of the horsepower-hour? Of the kilowatthour?

38. A heat engine operates on a cycle in the course of which it delivers 50,000 ft-lb of work to external systems during certain of the processes which make up the cycle and receives 30,000 ft-lb of work from the surroundings during the other processes of the cycle. The efficiency of the cycle is 15 per cent, and it is traversed 150 times per minute. What amount of heat is *received* from external systems in the course of the cycle? What is the *net* heat exchange with external systems during one complete cycle? What horsepower does the engine deliver?

39. A heat-engine cycle is composed of four closed-system processes, 1-2, 2-3, 3-4, and 4-1. If  ${}_1Q_2 = 75$  Btu,  ${}_2Q_3 = -5$  Btu,  ${}_3Q_4 = -48$  Btu, and  ${}_4Q_1 = -2$  Btu and the cycle is traversed three times per second, calculate its efficiency and the horsepower output.

40. What is the efficiency of the cycle described in Prob. 5?

41. A heat-engine cycle is composed of three maximum-work closed-system processes. An isothermal expansion begins at  $p_1 = 100$  psia,  $V_1 = 1$  ft<sup>3</sup>,  $t_1 = 1500^\circ\text{F}$ , and ends at  $p_2 = 20$  psia. The next, a constant-pressure process, ends at  $V_3 = 1$  ft<sup>3</sup>. The process that closes the cycle takes place at constant volume. If the system is composed of (a) gas  $W$ , (b) gas  $X$ , (c) gas  $Y$ , (d) gas  $Z$ , calculate the work and the heat flow accompanying each process, the net work of the cycle, and its efficiency. If a single source and a single refrigerator, each at respectively constant temperature, are employed, what minimum temperature is possible for the former, what maximum temperature for the latter?

42. In Prob. 41 consider that, owing to friction, the amount of work delivered during the isothermal expansion is reduced by 10 per cent and the amount of work received from external systems during the constant-pressure compression is increased in the same ratio. The constant-volume process is still a maximum-work process. How does this change affect the efficiency of the cycle when each of the four gases constitutes the working substance?

### Symbols

$A$  area; also, a constant

$B$  a constant

$c_p$  specific heat at constant pressure

$c_v$  specific heat at constant volume



$C$	a constant
$e$	stored energy of a system of unit mass, in general (thermal units)
$E$	stored energy of a system, in general (thermal units)
$h$	enthalpy of a system of unit mass (thermal units)
$H$	enthalpy of a system (thermal units)
$J$	proportionality factor
$k$	a constant ratio
$p$	pressure, psi
$P$	pressure in general; also, in psf
$Q$	heat flow (thermal units)
$Q_S$	rate of heat flow, from source (thermal units)
$Q_R$	rate of heat flow, to refrigerator (thermal units)
$t$	scalar temperature
$T$	absolute temperature
$u$	energy stored as thermal energy in unit mass; specific internal energy (thermal units)
$U$	energy stored as thermal energy in a system; internal energy (thermal units)
$v$	volume of unit mass; specific volume
$V$	volume of a system
$W$	work; also, rate of work delivery

*Greek letters*

$\eta$	efficiency of a heat engine
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*Subscripts*

max	maximum
$p$	constant pressure
$v$	constant volume

## CHAPTER 3

### THE FIRST LAW AND THE OPEN SYSTEM

**3:1. Stored Energy of the Open System.** The open system has been described in a manner such as to permit the flow of matter as well as of heat and work across its boundaries. For that reason the open-system process is called a *flow* process, while the process which involves a closed system is termed a *nonflow* process. From the use of the word flow it may be inferred that motion may no longer be ignored as in the case of the simple closed system and that account must be taken of energy stored in the system by reason of that motion. The amount of this form of stored energy may be measured in terms of the work required to start the system from rest and give it the designated velocity. Thus velocity is an additional property concerning which information must be at hand in dealing with an open system. It is not, however, one of the properties included in any equation of state of the pure substance and therefore cannot be established from the values of other properties alone; it must be individually stated or calculable.

In calculating the work required to impart motion to a body (and thereby the energy stored in the body by reason of its motion) we return to the laws of motion and find that

$$F = ma$$

where, if  $m$  is the mass in slugs and  $a$  is the acceleration in feet per second per second,  $F$  is the force required to impart that acceleration in pounds. If the time interval is short, the acceleration is constant and equal to  $d\bar{V}/dt$  (the instantaneous change of velocity with respect to time),  $dl$  is the distance traversed, and  $\bar{V} = dl/dt$ . But the work delivered to the body during this time interval is

$$F dl = ma dl$$

and

$$a = \frac{d\bar{V}}{dt} = \frac{d\bar{V}}{dl} \frac{dl}{dt} = \frac{d\bar{V}}{dl} \bar{V} = \frac{\bar{V} d\bar{V}}{dl}$$

Thus

$$dW = F dl = m\bar{V} \left( \frac{d\bar{V}}{dl} \right) dl = m\bar{V} d\bar{V} = d \left( \frac{m\bar{V}^2}{2} \right)$$

or

$$W = \frac{m\bar{V}^2}{2} = \Delta E$$



For a unit-weight (1-lb) system the energy stored by reason of its motion is therefore  $\bar{V}^2/2g$ .

Although gravity may usually be neglected, it is occasionally necessary to consider its effects. In this case the energy stored is the work required to elevate the system from the datum level, or the product of its weight and the change in elevation. In the case of unit weight the energy storage is simply the elevation, denoted by  $z$ .

Thus, for the slightly less simple system for which motion and gravity are taken into account (although capillarity, magnetism, and electricity are still ignored),

$$e = u + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \quad (3:1)$$

**3:2. Work and the Open System.** Work may cross the boundaries of the open system owing to a movement of those boundaries (an expansion or a contraction of those boundaries) as in the case of the closed system.

The flow of work across the boundary may also be due to paddle-wheel action as in the case of the closed system, but, for the open system, work may not only *enter* but also *leave* the system by this method under certain conditions and subject to certain limitations. For if the flow is continuous and follows a definite pattern throughout the system, it may be used to do work *on* the paddles and the system may in this manner deliver work to external systems.

The fluid that enters across the boundaries of the open system does so against the resistance offered by the pressure of the system at the point of entry; this requires that work be done on the system to force this entry. The system itself does work in ejecting fluid which crosses its boundaries in an outward direction. This type of work is called *flow work*.

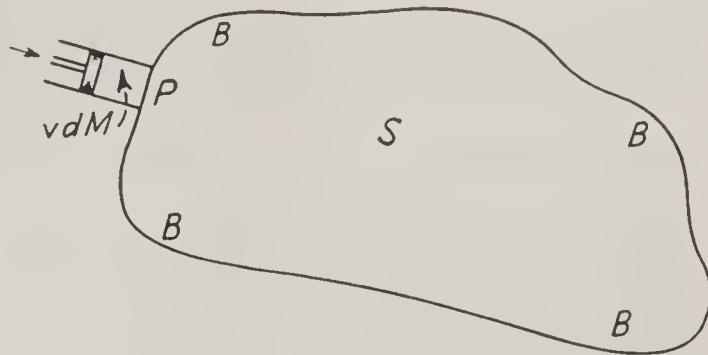


FIG. 3:1. Flow work.

For the purpose of convenient reference, the work of the open system exclusive of flow work will be called *external work*, and the symbol  $W$  will be used to represent it; external work may include work flow produced by either or both of the methods discussed in the first two paragraphs of this article.

**3:3. Flow Work.** In Fig. 3:1 is shown an elementary weight  $dM$  of fluid which is about to enter a large system  $S$  across its boundaries  $B$ . The flow work may be calculated as that which the piston shown in the sketch must perform to force that entry. Because of the relative size of  $S$  and  $dM$ , the pressure of the large system will not change appreciably as

the element of fluid is introduced. Since the boundary is assumed entirely permeable, it will not offer resistance of its own to the passage of  $dM$  and the piston will therefore operate against the constant pressure  $P$  (the local pressure of the large system at the point of entry). The volume swept through by the piston is  $v dM$ , and thus the work it performs is  $Pv dM$ . For the passage of a finite quantity of fluid,

$$\text{Flow work} = \int Pv dM \quad (3:2)$$

With respect to the system  $S$  this flow work is negative at any point of entry, positive at points of exit from the system.

*Example 3:3.* An open system simultaneously receives 1 lb of a substance having an equation of state as in Example 1:10 and, at a second point on its boundary, rejects the same weight of the same substance. At the point of entry the pressure and temperature of the system are, respectively, 50 psia and 300°F and remain constant at these values during the entry. At the point of exit the pressure and temperature are 20 psia and 130°F and are also constant with time. Calculate (a) the flow work at entrance, (b) the flow work at exit, and (c) the net flow work per pound of fluid passing through the system.

*Solution:*

(a) At entry,  $P_1 = (20)(144) = 7200$  psfa;  $v_1 = CT_1/p_1 = (0.37)(760)/50 = 5.62$  ft<sup>3</sup>/lb.

$$\text{Flow work at entry} = - \int_0^1 P_1 v_1 dM = -(7200)(5.62) \int_0^1 dM = -40,500 \text{ ft-lb/lb}$$

The negative sign is introduced to accord with the convention as to the sign of work,

(b) At exit,  $P_2 = (20)(144) = 2880$  psfa;  $v_2 = (0.37)(590)/20 = 10.9$  ft<sup>3</sup>/lb.

$$\text{Flow work at exit} = \int_0^1 P_2 v_2 dM = (2880)(10.9)(1) = 31,400 \text{ ft-lb/lb}$$

(c) The net flow work =  $-40,500 + 31,400 = -9100$  ft-lb per pound of fluid.

**3:4. The First Law and the Open System.** As the system  $S$  of Fig. 3:1 receives the element of fluid  $dM$ , its mass will change, as will also, in general, its total store of energy. This change in stored energy, according to the First Law as it applies to a process, must have derived directly from energy that crossed the system boundaries during the time required to introduce  $dM$ . This energy may be summarized to include work  $W$  that crossed the boundaries at points other than the point of entry of  $dM$ , flow work which accompanied the entry of  $dM$ , heat flow across any section of the boundary as  $dM$  was introduced, and the stored energy of  $dM$  itself as it was pushed across the boundary to become a part of system  $S$ . Expressing the change of stored energy of the system as being due to these effects in the form of an equation, we have



$$\begin{aligned}
dE &= -\frac{\partial W}{J} + Pv dM + \partial Q + \left(u + \frac{\bar{V}^2}{2Jg} + \frac{z}{J}\right) dM \\
&= -\frac{\partial W}{J} + \partial Q + \left(u + \frac{Pv}{J} + \frac{\bar{V}^2}{2Jg} + \frac{z}{J}\right) dM \\
&= -\frac{\partial W}{J} + \partial Q + \left(h + \frac{\bar{V}^2}{2Jg} + \frac{z}{J}\right) dM
\end{aligned} \tag{3:3}$$

**3:5. Steady Flow.** Many engineering applications of the open system will occur to the reader. For instance, in the case of the steam turbine the boundaries are fixed in position and are formed by the turbine casing and sections across the inlet and exhaust passages. Work crosses those boundaries along the turbine shaft (as *shaft work*), and heat may pass across them as due to radiation to the surroundings. Steam enters at the inlet and is discharged at lower pressure at the exhaust end of the turbine. This steam carries with it certain stored energy amounts and performs flow work on the system at entry, receiving flow work from the system as it is discharged.

The use of Eq. (3:3) in analyzing such processes is greatly simplified if *steady-flow* conditions are assumed. This requires that:

1. The time rate of fluid entry (mass per unit time) is the same as that of exit from the system.
2. The fluid at entry has a uniform composition, state, and velocity that does not change with time.
3. The same is also the case at exit.
4. The state of the fluid at any given point within the system does not change with time although different points within the boundaries may differ in their states.
5. The time rate of heat flow across the boundaries of the system is constant.
6. The same is true of the time rate of work flow across those boundaries.

For the purpose of applying Eq. (3:3) to the steady-flow process, it is convenient to select a time interval during which 1 lb of the fluid will enter (and 1 lb leave) the system. Requirement 4 above assures that there will be no change in the energy stored in the system with time and therefore  $E_2 - E_1 = 0$ . Designating the conditions at the entrance by the subscript <sub>1</sub> and those at exit by <sub>2</sub>, Eq. (3:3) becomes

$$0 = -\frac{{}_1W_2}{J} + {}_1Q_2 + h_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} - h_2 - \frac{\bar{V}_2^2}{2Jg} - \frac{z_2}{J} \tag{3:4}$$

where  ${}_1W_2$  = work (other than flow work) which system performs on external systems during time required for unit weight of fluid to enter system, ft-lb

${}_1Q_2$  = heat that system receives in same time interval, Btu

$h_1, h_2$  = specific enthalpies of the fluid at entrance and at exit states, respectively

$\frac{\bar{V}_1^2}{2Jg}, \frac{\bar{V}_2^2}{2Jg}$  = specific stored energies due to motion of fluid entering and leaving system, respectively

$z_1, z_2$  = specific stored energies due to elevation (gravity) at same points

When Eq. (3:4) is rearranged, it assumes the typical form which is called the *steady-flow energy equation*,

$$h_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} + {}_1Q_2 = h_2 + \frac{\bar{V}_2^2}{2Jg} + \frac{z_2}{J} + \frac{{}_1W_2}{J} \quad (3:5)$$

The elevation terms,  $z_1/J$  and  $z_2/J$ , are often dropped from this equation as representing energy amounts too small to be significant in comparison with the energy quantities represented by the other terms. In fact,

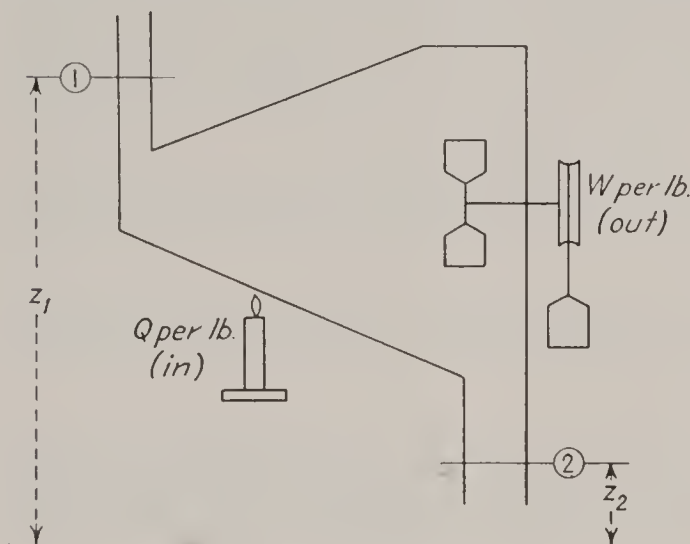


FIG. 3:2. Steady flow.

differences in elevation between entrance and exit are usually not stated even when it is intended that Eq. (3:5) is to be applied to the solution of the problem. Figure 3:2 is illustrative of the open-system steady-flow process. In accordance with the notation of Eq. (3:5), the entry section is designated as 1, the exit as 2.

*Example 3:5.* Assume that steady-flow conditions existed between entrance and

exit of the system described in Example 3:3, that the velocity at entrance was 100 fps, and that the point of entry was 5 ft above the exit.

- Calculate the total energy introduced into the system at the point of entry per pound of fluid entering and the specific enthalpy of the entering fluid.
- If the process was adiabatic and no external work was done, what was the velocity of the fluid at exit?
- If the process was adiabatic and the velocity at exit was 500 fps, calculate the energy that was transferred to other systems as work per pound of fluid passing through the system, *i.e.*, the external work per pound of fluid flow.
- If no external work was done and the velocity at exit was the same as at entrance, how much heat was transferred per pound of fluid flow and in what direction?

*Solution:*

$$(a) \ u_1 = 16 + (0.46)(50)(5.62) = 145 \text{ Btu/lb.}$$

$$e_1 = u_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} = 145 + \frac{100^2}{(2)(778)(32.2)} + \frac{5}{778} = 145 + 0.2 + 0.006 = 145.2 \text{ Btu}$$



It will be noted that this quantity is relative to the more or less arbitrary bases with reference to which  $u$ ,  $V$ , and  $z$  are evaluated. For instance, in this case  $z$  has been referred to a datum level corresponding to the elevation of the exit section, and it will be noted that the stored energy due to elevation is so small that it has been dropped from the total as not significant. Naturally, if the stored energy at any other point in the system, such as the exit, is the subject of calculation, the same bases must be retained for the computation of each term. *With respect to these datum levels*, the total energy introduced into the system at the point of entry of the fluid is the sum of the energy stored in the pound of fluid that is entering and the (flow) work performed on the system in forcing its entry, or  $145.2 + (40,500/778) = 197.2$  Btu per pound of fluid entering. The specific enthalpy of the fluid at entry is

$$h_1 = 16 + 0.645pv = 16 + (0.645)(50)(5.62) = 197 \text{ Btu/lb} \quad [\text{Ex. 2:9(f)}]$$

(b) Applying Eq. (3:5),  ${}_1Q_2 = 0$  (the flow was adiabatic), and  ${}_1W_2 = 0$  (no external work was performed). The potential energy terms  $z_1/J$  and  $z_2/J$  may be dropped from the equation since  $z_1/J$  was insignificant and  $z_2/J$  is zero. From (a),  $h_1 = 197$  Btu and  $\bar{V}_1^2/2Jg = 0.2$  Btu. Then

$$\begin{aligned} h_2 &= 16 + (0.645)(20)(10.9) = 156.7 \text{ Btu} \\ \bar{V}_2^2 &= 2Jg \left( h_1 + \frac{\bar{V}_1^2}{2Jg} + {}_1Q_2 - h_2 - \frac{{}_1W_2}{J} \right) \\ &= (2)(778)(32.2)(197 + 0.2 + 0 - 156.7 - 0) \\ &= (50,000)(40.5) = 2,025,000 \end{aligned}$$

or

$$\bar{V}_2 = 1423 \text{ fps}$$

(c)  ${}_1Q_2 = 0$ ;  $h_1 = 197$  Btu;  $\bar{V}_1^2/2Jg = 0.2$  Btu;  $h_2 = 156.7$  Btu.

$$\begin{aligned} \frac{\bar{V}_2^2}{2Jg} &= \frac{500^2}{50,000} = 5 \text{ Btu} \\ {}_1W_2 &= J \left( h_1 + \frac{\bar{V}_1^2}{2Jg} + {}_1Q_2 - h_2 - \frac{\bar{V}_2^2}{2Jg} \right) = 778(197 + 0.2 + 0 - 156.7 - 5) \\ &= (778)(35.5) = 27,600 \text{ ft-lb} \end{aligned}$$

The positive sign indicates that work (other than flow work) would have been transferred to other systems as a result of this steady-flow process.

$$(d) \quad {}_1W_2 = 0; \quad \frac{\bar{V}_2^2}{2Jg} = \frac{\bar{V}_1^2}{2Jg} = 0.2 \text{ Btu.}$$

$${}_1Q_2 = h_2 + \frac{\bar{V}_2^2}{2Jg} + \frac{{}_1W_2}{J} - h_1 - \frac{\bar{V}_1^2}{2Jg} = 156.7 + 0.2 + 0 - 197 - 0.2 = -40.3 \text{ Btu}$$

The negative sign indicates that this heat passed out of the system.

**3:6. The Bernoulli equation** is the steady-flow equation [Eq. (3:5)] as it applies to flow through a “conservative” system when no external (shaft) work is performed. For any real fluid, one of the properties that is associated with a given state is its viscosity. This property expresses the magnitude of the forces that are set up because of friction between the molecules due to their motion relative to each other. Because of viscosity, some shearing stresses will exist in any real fluid, but these stresses

are sometimes so small that they may be ignored; this is especially true with respect to gases. A system composed of a hypothetical substance which does not have viscosity and in which these shearing stresses are therefore not present is called a *conservative system*. A conservative system could apply force to an adjacent system only in a direction normal to its boundaries; as it slides over the walls of the passage or across other portions of the fluid, an element of the fluid would not be retarded by friction. As it expanded in volume, the work performed by this element of fluid would, in the absence of friction, be a maximum.

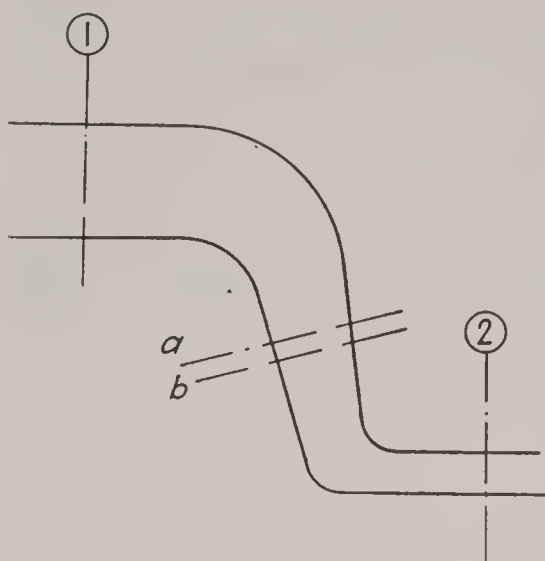


FIG. 3:3. Steady flow and the conservative system.

Let us consider a conservative system which consists of a unit mass of fluid as it passes through an open system in steady flow. The channel through which this flow takes place is pictured in Fig. 3:3, and it is our purpose to study the change in state of this unit mass as it moves between section 1 and section 2 of the channel. To aid in our study, we shall consider the segment of the passage that lies between

sections *a* and *b*, which are an infinitesimal distance apart. Applying Eq. (3:5) to this section of the passage by expressing it in differential form, we have, when no external work (work other than flow work) is performed,

$$J dh + d\left(\frac{\bar{V}^2}{2g}\right) + dz - J \partial Q = 0$$

Or, since  $Jh = Ju + Pv$ ,

$$J du + P dv + v dP - J \partial Q + d\left(\frac{\bar{V}^2}{2g}\right) + dz = 0 \quad (1)$$

The unit mass which we are studying constitutes a closed system. It is moving and therefore may change in velocity and in elevation, but velocity and elevation are purely relative quantities, and an observer who was stationed "on board" the element and moved with it would see no change in these properties; to him, it would seem merely that external systems were changing in velocity and in height. For him, the system would be a simple system and one which, because it was a conservative system, could carry out only maximum-work processes. He would therefore apply Eq. (2:5) to an analysis of its behavior; in addition, he would be justified in substituting  $P dv$  for  $\partial W$  in that equation. Or, rearranging,

$$J du + P dv - J \partial Q = 0$$



Removing these terms from (1), we have

$$v dP + d\left(\frac{\bar{V}^2}{2g}\right) + dz = 0 \quad (3:6)$$

This is *Bernoulli's equation*. Although it applies to a conservative system, it is often used to approximate flow relations for real fluids.

Another concept that is occasionally of importance in engineering is that of the *perfect fluid*. The perfect fluid has all of the characteristics required of the fluid of a conservative system and, in addition, is incompressible. When Eq. (3:6) is applied to an incompressible fluid, integration gives

$$Pv + \frac{\bar{V}^2}{2g} + z = \text{const} \quad (2)$$

or, dividing by  $v$ ,

$$P + \frac{\rho \bar{V}^2}{2} + wz = \text{const} \quad (3:7)$$

in which  $\rho$  is the mass density of the fluid, in slugs per cubic foot, and  $w$  is its weight density, in pounds per cubic foot. The constant is the unvarying *total head* (total "pressure") at all points along the channel of flow of a perfect fluid when no shaft work is performed.

Bernoulli's equation in the special form of Eq. (3:7) is often applied by the engineer to approximate flow relations for liquids, as in hydraulics, since they are characteristically compressible in only very slight degree. At times, when the changes in pressure are relatively very small, it is applied to the study of gas flows in order to simplify the mathematical treatment.

*Example 3:6.* Water flows vertically downward in a converging tube. At a point 100 ft below the entrance its velocity is 40 fps, and its pressure is 50 psig. At 500 ft below the entrance the pressure is 180 psig. Assume that the density of the water is constant at 62.5 lb/ft<sup>3</sup> and that this is a conservative system. Calculate the velocity at the lower section (a) by applying the Bernoulli equation and (b) by using the steady-flow energy equation.

*Solution:*

$$v = \frac{1}{62.5} = 0.016; dP = 144(180 - 50) = 18,720 \text{ psf}; dz = -400 \text{ ft}$$

$$(a) \quad v dP + d\left(\frac{\bar{V}^2}{2g}\right) + dz = (0.016)(18,720) + d\left(\frac{\bar{V}^2}{2g}\right) - 400 = 0 \quad [\text{Eq. (3:6)}]$$

$$d\left(\frac{\bar{V}^2}{2g}\right) = \frac{\bar{V}_2^2}{2g} - \frac{\bar{V}_1^2}{2g} = \frac{\bar{V}_2^2}{2g} - \frac{40^2}{64.4} = 400 - (0.016)(18,720) = 100$$

$$\bar{V}_2^2 = 64.4(100 + 24.8) = 8050 \text{ or } \bar{V}_2 = 89.7 \text{ fps}$$

(b) Since this is a conservative system,  $\partial Q - du - P dv/J = 0$ . But  $dv = 0$ , and therefore  $\partial Q = du$ . If, in substitution in Eq. (3:5), any value of  ${}_1Q_2$  is substituted,

it will be balanced by an equal difference between  $u_2$  and  $u_1$  (which form a part of  $h_2$  and  $h_1$ ) so that no effect will result in the calculation of  $\bar{V}_2$ , the required quantity. For simplicity, we shall assume that there is no heat flow and that consequently  $u_2 = u_1$ . In that case,

$$h_2 - h_1 = \frac{\Delta(Pv)}{J} = \frac{v \Delta P}{J} = \frac{0.16(180 - 50)(144)}{778} = 0.385 \text{ Btu}$$

Applying Eq. (3:5),

$$\begin{aligned} \bar{V}_2^2 &= 2Jg \left( h_1 - h_2 + \frac{\bar{V}_1^2}{2g} + \frac{z_1 - z_2}{J} + {}_1Q_2 - \frac{{}_1W_2}{J} \right) \\ &= 50,000 \left( -0.385 + \frac{40^2}{50,000} + \frac{400}{778} + 0 - 0 \right) \\ &= 50,000(-0.385 + 0.032 + 0.514) = (50,000)(0.161) = 8050 \end{aligned}$$

or

$$\bar{V}_2 = 89.7 \text{ fps}$$

An interesting feature of the solution of this example is the calculation of the change of enthalpy as  $\Delta Pv/J$ . Expressed in the form of a differential this becomes  $dh = v dP/J$ . Examining further, it is noted that  $dh = d(u + Pv/J) = du + P dv/J + v dP/J$ . For the maximum-work adiabatic process,  $\partial Q = 0 = du + P dv/J$  and therefore  $dh = v dP/J$ . In the case of an incompressible fluid (and most liquids are compressible only in negligible degree), this equation furnishes a simple method of calculating enthalpy changes during the maximum-work adiabatic process. The equation is valid, of course, even for gas systems that change in volume during this type of process but is less readily applied.

**3:7. The Continuity Equation of Steady Flow.** In steady flow, the volume of flow passing any given section of the channel in unit time may be calculated either as the product of the mass rate of flow past that section and the (average) specific volume of the fluid as it passes the section or as the product of the cross-sectional area of the channel and the (average) velocity with which the fluid passes the section. Equating,  $Mv = A\bar{V}$ , and, rearranging,  $M = A\bar{V}/v$ . Since the flow is steady, requirement (a) of Art. 3:5 applies and  $M$  has the same value for all sections along the channel. Thus we may write

$$M = \frac{A\bar{V}}{v} = \frac{A_1\bar{V}_1}{v_1} = \frac{A_2\bar{V}_2}{v_2} = \text{const} \quad (3:8)$$

in which the subscripts refer to successive sections normal to the direction of flow and  $A$  refers to the areas of those sections. Equation (3:8) is called the *continuity equation of steady flow*. It is often useful in providing a link between the velocity, the cross-sectional area of the passage, and those properties of the system which are known and may be used to enter the equation of state and solve it to obtain the specific volume.

It is sometimes possible to select sections across all parts of which the velocity is the same. When an average velocity only is obtainable, it is customary to use this average velocity in the steady-flow energy equation



although this procedure introduces some inaccuracy since the velocity is squared in the kinetic-energy term. If the error is considered too large to be ignored, the section may be subdivided into elementary areas over each of which the velocity varies negligibly and the kinetic energies of the respective elementary flows may be integrated.

*Example 3:7.* (a) In part *b* of Example 3:5 assume a flow rate of 1 lb/sec, and calculate the necessary areas of the inlet and exit passages. (b) At one point between the entrance and the exit, the pressure of the fluid is 26.5 psia, and its temperature is 173°F. What is the velocity at this point, and what is the necessary passage area for a flow rate as in part *a*?

*Solution:*

(a) From Eq. (3:8),

$$A_1 = \frac{M_1 v_1}{\bar{V}_1} = \frac{(1)(5.62)}{100} = 0.0562 \text{ ft}^2$$

$$A_2 = \frac{M_2 v_2}{\bar{V}_2} = \frac{(1)(10.9)}{1423} = 0.0077 \text{ ft}^2$$

(b) This point in the flow will be designated by the subscript 0. Then

$$v_0 = \frac{CT_0}{p_0} = \frac{(0.37)(173 + 460)}{26.5} = 8.85 \text{ ft}^3/\text{lb}$$

$$h_0 = 16 + 0.645 p_0 v_0 = 16 + (0.645)(26.5)(8.85) = 167.3 \text{ Btu/lb} \quad [\text{Ex. 2:9}]$$

$$\begin{aligned} \bar{V}_0^2 &= 2Jg \left( h_1 + \frac{\bar{V}_1^2}{2Jg} + {}_1Q_2 - h_2 - \frac{{}_1W_2}{J} \right) = 50,000(197 + 0.2 + 0 - 167.3 - 0) \\ &= (50,000)(29.9) = 1,495,000 \text{ or } \bar{V}_0 = 1230 \text{ fps} \end{aligned}$$

$$A_0 = \frac{M_0 v_0}{\bar{V}_0} = \frac{(1)(8.85)}{1230} = 0.0072 \text{ ft}^2$$

It will be observed that, although the values of the pressure, specific volume, temperature, and velocity at point 0 were intermediate between the values of the corresponding properties at the points of entry into and exit from the open system, the area of the passage that confines the system and through which the flow is taking place is less at that point than at either entrance or exit. The methods used in solving this problem have an application to the design of nozzles, which are devices for utilizing the stored energy of the fluid to give it increased velocity, and to the design of diffusers, which have the opposite effect. The basis of selection of the properties at the intermediate point 0 will be discussed in a later chapter of this text.

**3:8. The Steady-flow Heat Engine.** The elementary steam-power-plant circuit diagramed in Fig. 3:4 is an excellent example of the steady-flow heat engine. Its efficiency as a heat engine may be obtained by applying either Eq. (2:14) or Eq. (2:15). As the fluid passes around the circuit, it may receive or discharge heat, perform or accept work, in devices that are each individually designed for the processes which are to be carried out in them. It thus does not suffer from the serious handicaps that existed in the case of the heat engine described in Chap. 2. Taken as a whole, the fluid enclosed within this steady-flow heat engine constitutes a closed system, but it differs from the type of closed system dis-

cussed in Chap. 2 since its properties are not uniform throughout the system and since velocity may be an important property at certain points in the system.

Although as a whole this type of heat engine constitutes a closed system, it may also be considered as an *open-system cycle* in the sense that an element of the fluid in making the circuit eventually returns to its initial state. The circuit may conveniently be divided into a number of open systems (in this case, four) for the purpose of examining the individual steady-flow processes that make up the complete cycle.

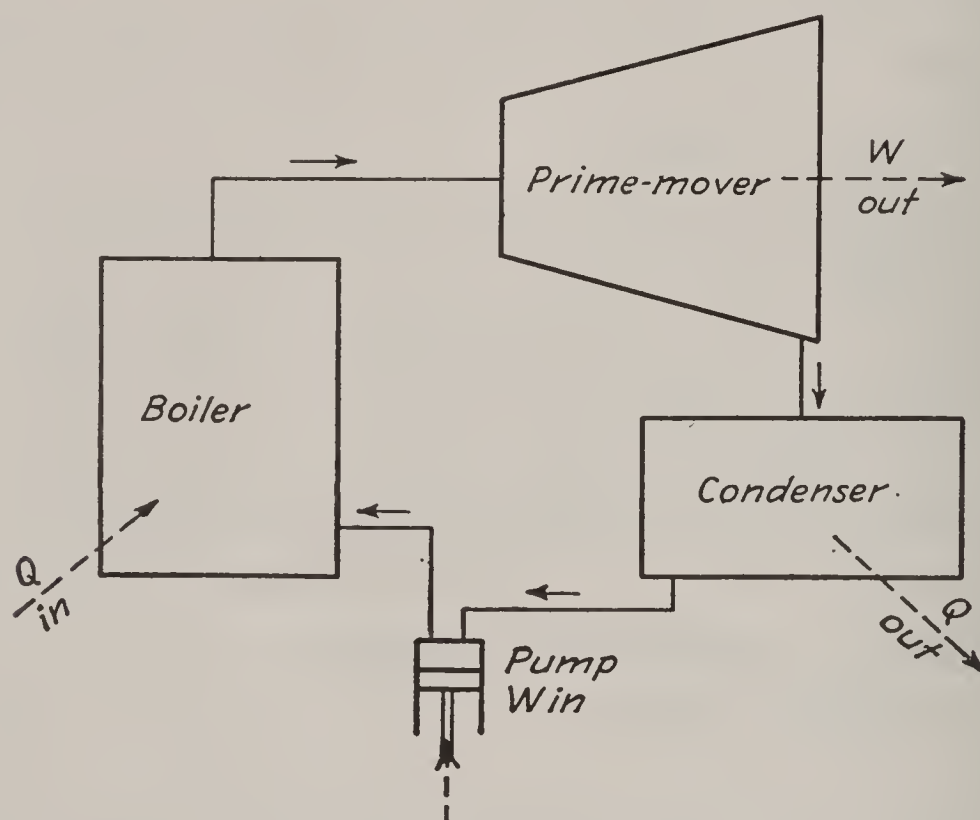


FIG. 3:4. A steady-flow heat engine.

In Fig. 3:4 the boiler and condenser are examples of the *heat exchanger*, which has as its object the heating or cooling of a fluid. When a heat exchanger is isolated as an open system, the differences in kinetic and potential energy of the fluid at entrance and at exit will ordinarily be negligible and no external work will be performed by the fluid in passing through the system. Applying the steady-flow energy equation, it then develops that the heat flow per pound of fluid entering (and leaving) is

$${}_1Q_2 = h_2 - h_1 \quad (3:9)$$

in which  $h_1$  and  $h_2$  are the specific enthalpies of the fluid at entry and exit, respectively.

The steady-flow energy equation may similarly be used to analyze the action of the prime mover. If that unit is a turbine, the boundaries of the open system, between sections across the inlet and exhaust passages, are fixed. Neglecting radiation (heat flow) and treating changes in kinetic



and potential stored energy between entrance and exit as negligible, it develops that

$${}_1W_2 = J(h_1 - h_2) \quad (3:10)$$

in which  ${}_1W_2$  is the external work (shaft work) per pound of fluid flow and  $h_1$  and  $h_2$  are the specific enthalpies of the fluid at entrance to and exit from the turbine, respectively. This equation, based on the First Law, does not limit the amount of work that may be done to any maximum amount for it makes no attempt to specify what relation shall exist between  $h_2$  and  $h_1$  in Eq. (3:10). Considering the relative preciousness of work and of heat, it will occur to the reader that some such limitation should apply. The discussion of this limitation will be left to a later chapter when we shall be better equipped to deal with the subject.

The form of Eqs. (3:9) and (3:10) may cause the reader to gain the impression that enthalpy represents stored energy of the system. He is again reminded that this is not the case. Enthalpy is merely a composite property, a property that is of great usefulness as is indicated in these equations and others previously developed but not one that measures the storage of energy in the system.

Any of the open systems that are discussed above may be subdivided into smaller systems for the purpose of more detailed analysis as seems desirable. For instance, in the case of the turbine a system may be selected that is appropriate for the study of the flow through a nozzle which is bounded by the walls of the nozzle and sections across the flow passages just ahead of and immediately after the nozzle. The change of kinetic energy will obviously be significant in this case, though the flow may be considered to be adiabatic and differences in elevation may be ignored. No external work is involved and the steady-flow energy equation assumes the form

$$\frac{\bar{V}_2^2}{2g} - \frac{\bar{V}_1^2}{2g} = J(h_1 - h_2) \quad (3:11)$$

The left side of this equation is the change of kinetic energy, and since this is a form of energy that can be completely converted into work, it will again be evident that  $h_2$  must be related to  $h_1$  in some manner as yet undisclosed.

**3:9. Quasi-steady Flow.** In the preceding article the steady-flow energy equation was applied to the turbine prime mover because it was the simplest type of prime mover for the purpose of demonstrating the steady-flow principle. If the prime mover is of the reciprocating-engine type, the boundaries of the open system that is formed are no longer fixed but pulsate periodically between certain limiting positions as shown in Fig. 3:5. Requirement 4 of Art. 3:5 is not satisfied though the state at any point in the open system does follow a definite change pattern and

returns periodically to a given state. This is called *quasi-steady flow*. The steady-flow energy equation may be applied to flow of this kind if receivers are provided as shown in Fig. 3:5 to damp out the oscillations in the state of the fluid at the entry and exit sections. Requirement 4 of Art. 3:5 is therefore not rigorous in limiting the application of the steady-flow energy equation.

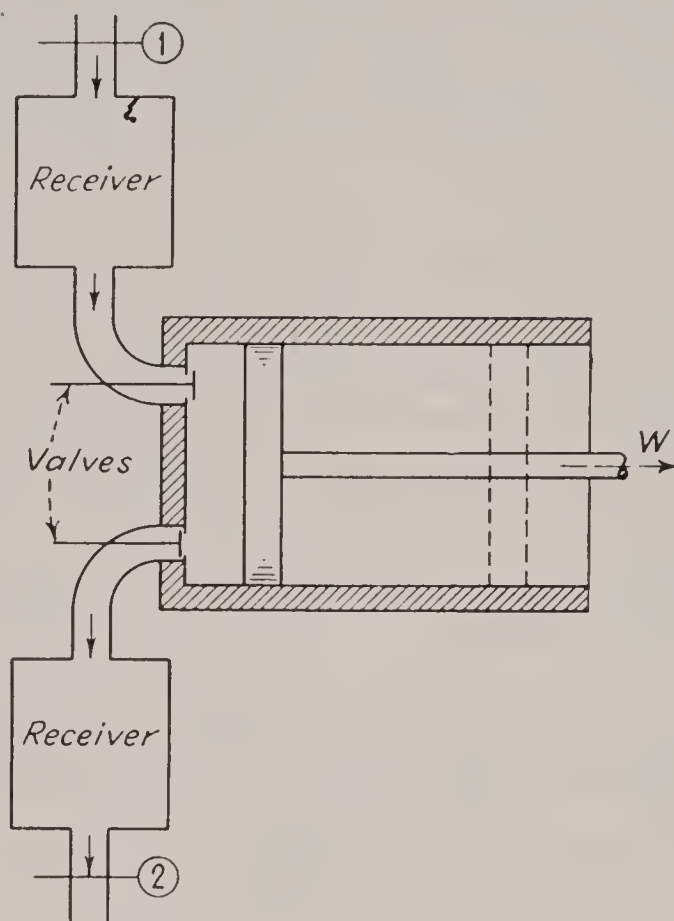


FIG. 3:5. Quasi-steady flow.

The external work is again shaft work as for the turbine but is in this case exchanged with other systems owing to a translation rather than a rotation of the shaft. The work delivery of the turbine was smooth, steady, and continuous, while  ${}_1W_2$  for the engine must be interpreted as the difference between the rate at which work leaves the system as its boundaries expand and the rate at which it reenters the system owing to the contraction that accompanies every pulsation. None the less, if the same assumptions are made (adiabatic flow, no significant differences in kinetic or potential energy between entrance and exit), it will be found that Eq. (3:10) will apply to the reciprocating engine as well as to the turbine prime mover.

When the same methods are applied to the pump shown in the flow diagram of Fig. 3:4, the same assumptions will be found to apply and Eq. (3:10) will again develop. In this case,  ${}_1W_2$  being negative, it is evident that  $h_2$  is greater than  $h_1$ .

### Problems

1. At entry to a receiver a gas has a velocity of 1000 fps, and at exit its velocity is 100 fps. The exit is 10 ft above the entrance, and  $\Delta e$  is zero between entrance and



exit states. What is the change of temperature between entrance and exit if the gas is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

2. A teakettle contains 5 lb of water and 0.01 lb of steam, both at 14.7 psia and 212°F. The specific volume of the water is 0.016 ft<sup>3</sup>/lb, and its internal energy is 180 Btu/lb. The similar values for the steam are 26.8 ft<sup>3</sup>/lb and 1077.6 Btu/lb. The kettle is placed on a stove, and heat is supplied until 1 lb of the water has boiled away, escaping with negligible velocity through the kettle spout to the atmosphere. What is the amount of external work? What is the amount of flow work? Neglecting the volume of the water which has boiled away, what is  $\Delta E$  for the open system consisting of the kettle contents? If heat losses to the atmosphere through the kettle walls are neglected, what heat flow takes place?

3. At entrance to a horizontal constricted passage, the pressure of a gas which is in steady flow through the channel is 100 psia, its temperature is 100°F, and its velocity is 100 fps. At the narrowest section, the pressure is 80 psia, and the temperature is 40°F. There is no heat flow through the walls of the channel between the two sections, nor is there any external work. What is the net flow work per pound of gas if it is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

4. In Prob. 3, what is the velocity at the narrowest section of the passage, for each of the four gases? In each case, what is the ratio of the cross-sectional area of the passage at its narrowest section to its area at the entrance?

5. At entrance to an open system, the pressure is 60 psia, the temperature is 120°F, and the velocity is 800 fps. At exit,  $p_2 = 100$  psia,  $t_2 = 260^\circ\text{F}$ . The flow is steady, and the exit is 3 ft above the entrance. The gas is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*. Answer the following questions:

(1) What amount of stored energy is introduced into the system at the entrance per pound of gas crossing that boundary?

(2) If the process is adiabatic and the velocity at exit is 200 fps, what is the external work per pound of gas flowing through the system?

6. In steady slow (at negligible velocity) flow through a horizontal pipe, a fluid passes through an orifice plate containing a small opening. There is no external work and the flow is adiabatic. The entrance section is well upstream, and the exit section is well downstream from the orifice. The pressure and temperature at entrance are 50 psia and 100°F; at exit the pressure is 20 psia. What is the temperature at exit if the fluid is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

7. A gas is in steady flow through an open system. The temperature of the gas is 600°F, and its velocity is 100 fps at entrance. The temperature at exit is 120°F, and the velocity is 300 fps. The flow is at the rate of 50 lb/min, and 10,000 Btu of heat leaves the system every hour. What horsepower does the system deliver as shaft work if the gas is (a) gas *W*; (b) gas *X*; (c) gas *Y*; (d) gas *Z*?

8. The temperature of an ideal gas is the same at entrance to and at exit from a passage, but the pressure drops from 75 to 25 psia. If the flow is steady and the velocities are the same at entrance and exit, what is the ratio of exit to entrance area?

9. At the throat of a nozzle the velocity of a gas is 1500 fps, and its specific volume is 4 ft<sup>3</sup>/lb. The cross-sectional area at the throat is 1 in.<sup>2</sup>, and at the exit it is 2.5 in.<sup>2</sup>. The specific volume of the gas at exit is 16 ft<sup>3</sup>/lb. What is the velocity at exit?

10. Liquid water (density = 62.4 lb/ft<sup>3</sup>) flows adiabatically through a horizontal converging tube. At a certain section its pressure is 100 psia, and its velocity is 20 fps. At a later section the velocity has become 50 fps. Assuming this to be a conservative system, what is the pressure at the second section?

11. In Prob. 10, if the second section had been 100 ft below the first, what would have been the pressure at that section?

12. Compressed air flows in an open line, horizontal and of constant diameter. At a

section near the entrance, the pressure of the air is 90 psia, its specific volume is  $2.5 \text{ ft}^3/\text{lb}$ , and its velocity is 100 fps. At a later section, the pressure is 85 psia, and the specific volume is  $2.3 \text{ ft}^3/\text{lb}$ . The specific internal energy decreased by 13.3 Btu between the sections. What heat flow (Btu per pound of air carried) took place between the two sections, and in what direction did it flow?

13. A boiler evaporates 50,000 lb of water per hour. At a section of the feedwater line entering the boiler, the enthalpy of the water is 68 Btu/lb, the velocity is 30 fps, and the elevation is 5 ft above the boiler-room floor. At a section of the steam line leaving the boiler, the enthalpy of the steam is 1200 Btu/lb, the velocity is 150 fps, and the elevation is 30 ft. If 75 per cent of the heat value of the coal (12,000 Btu per pound of coal) is used in heating the water and steam, how many pounds of coal are burned per hour?

14. A steam turbine receives steam having a specific enthalpy of 1250 Btu/lb. The rate of steam flow is 12,000 lb/hr, and the turbine delivers 800 kw. The heat loss by radiation may be considered negligible. The steam enters the turbine at 100 fps and leaves at a velocity of 500 fps. The exit section is 5 ft below the entrance. What is the enthalpy of the steam at exit from the turbine?

15. A steam engine receives 3000 lb of steam per hour at an enthalpy of 1195 Btu/lb and exhausts steam having an enthalpy of 1080 Btu/lb. The heat loss from the engine cylinder and the piping between the entry and exit sections is at the rate of 6000 Btu/hr. Assuming that the velocities and elevations at entrance and exit differ negligibly, what power does this open system develop?

16. The enthalpy of the steam as it enters a condenser is 1080 Btu/lb; that of the condensate at exit is 150 Btu/lb. Three thousand pounds of steam is condensed per hour. The velocity of the steam at entrance is 300 fps; of the condensate it is 30 fps. If the cooling water increases in temperature by  $50^\circ\text{F}$  in flowing through the condenser and 50,000 Btu of heat is radiated per hour directly to the atmosphere from the shell of the condenser, how many pounds of cooling water must be supplied per hour? Neglect differences in elevation. The specific heat of water is 1.

17. Derive an expression for the work required to operate a feedwater pump, per pound of water pumped, by applying Eq. (3:5). Assume inlet and outlet velocities and elevations equal, no heat transfer, that the system is a conservative system, and that the specific volume of the water remains constant as the pressure increases.

18. Steam flows through a small opening from a region of higher pressure to a chamber in which a lower pressure is maintained. If sections are chosen at a suitable distance on the two sides of the opening and the flow rate is small, the difference between upstream and downstream kinetic energy is small and may be ignored. If the flow is adiabatic, show that no change of enthalpy will result.

19. The specific enthalpy of the air as it leaves an air compressor is 47 Btu greater than as it entered. One thousand pounds of air is compressed per hour, 27 hp being needed to drive the compressor. Neglecting differences of velocity and elevation between entrance and exit, calculate the heat rejected to the cooling water jacket and the atmosphere per pound of air compressed.

20. One pound of  $\text{H}_2\text{O}$  flows around the circuit which is diagramed in Fig. 3:4. In the boiler it receives 850 Btu, in the condenser it gives up 700 Btu of heat. Radiation from the prime mover, the feedwater pump, and the various steam and water lines accounts for a heat loss of 25 Btu to the atmosphere. Work in the amount of 1 Btu is supplied to drive the feedwater pump as it pumps the pound of condensate into the boiler. What is the work output by the prime mover per pound of steam flow? What is the net work output of the heat engine per pound of flow? What is the efficiency of this steady-flow heat engine?



## Symbols

$a$	acceleration
$A$	cross-sectional area of a channel, normal to the direction of flow
$e$	stored energy of unit mass
$E$	stored energy of a system
$F$	force
$g$	acceleration due to gravity
$h$	specific enthalpy
$J$	proportionality factor
$l$	distance
$m$	mass, slugs
$M$	mass rate of flow
$p$	pressure, psi
$P$	pressure; pressure, psf
$Q$	heat flow per unit-mass rate of flow
$t$	time
$u$	specific internal energy
$v$	specific volume
$\bar{V}$	velocity
$w$	weight density
$W$	shaft work per unit-mass rate of flow
$z$	height; elevation above a datum level

*Greek Letters*

$\rho$	mass density
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## CHAPTER 4

### THE REVERSIBLE PROCESS AND THE REVERSIBLE CYCLE

**4:1. Thermodynamic Reversibility.** Continued reference has been made in these pages to the fact that work is a more valuable form of energy than is heat. The reader can scarcely have failed to arrive at the same conclusion, based on his own independent observation. Any process during which work is used to produce an effect that could have been produced, at least in part, by a flow of heat therefore falls short of thermodynamic perfection and represents a waste of energy in its more valuable form.

If, after the conclusion of a process, the system may be restored to its original state and all other systems returned to their original conditions as at the beginning of the original process, it may reasonably be concluded that no such wastage accompanied that process. In this case the process is said to be *thermodynamically reversible*. Reversibility therefore provides a test that can be applied to determine whether or not the process has been perfectly executed in the thermodynamic sense and thus to prove whether work or any form of energy which could have been changed completely into work (such as kinetic or potential mechanical energy, for example) has been used for purposes that could have been served by a flow of heat.

**4:2. Reversibility and the Closed-system Process.** Returning to the statement of what constitutes reversibility in a process, it is noted that not only must the system be restored to its original state but all other systems that were involved in the process must be returned to their original condition. This requires that:

1. *If an external system receives work during a reversible process, it must store the amount of energy equivalent to this work in some form such that it is available for return as work flow in the opposite direction and in undiminished amount during the contemplated return of all systems to their original states.* As an example of how this might be done, consider that the work performed on a piston by the expanding system could be used to give angular acceleration to a flywheel and thus to store kinetic mechanical energy in the external system, which here consists of the piston, flywheel, and connecting linkage. During the return process, work could pass from this external system as the flywheel decelerates. If all parts of this external system were frictionless, the work flow in the two directions would be the same and this requirement would be satisfied.



2. One of the requirements for the reversibility of a process is that it may be stopped at any point and the return to the original state for all systems involved made from that point. Therefore, *for any reversible process the path followed during the return process must retrace that traversed in the original process.*

3. *It must require exactly as much work from external systems to restore the system to its original state as was delivered to those external systems during the original process.* This means that the process must be a maximum-work process if the system is to be returned to its original state over the same path. Otherwise (a) less work than is represented by the area under the path on a  $PV$  diagram would be delivered by the system to external systems as the system expanded, (b) this area would represent the *minimum* amount of work (in the absolute sense) which these external systems would be called upon to return to the system in retracing the same path, and (c) an inequality would result. Maximum work requires that there shall be no degree of unrestrained expansion and no paddle-wheel work (friction) during a closed-system process.

4. *When heat flows to an external system during the process, that external system must store the equivalent amount of energy in a form and under conditions such that it can be returned as heat and in its full amount during the return process.* Since heat flows only in response to a differential of temperature and always from the system at higher to that at lower temperature, it is clear that no process involving the flow of heat can be truly reversible. However, it may approach reversibility as a limit as the differential of temperature between the systems which exchange heat decreases.

A review of the preceding paragraphs will indicate that *friction, unrestrained expansion, and the flow of heat across a finite temperature interval* will prevent the attainment of reversibility in a closed-system process. These factors are always present in any real process, and therefore no real process can be completely reversible and thus perfectly executed in the thermodynamic sense. But as the effects of friction are reduced toward zero by improved methods of lubrication, as the effects of unrestrained expansion are minimized by slow piston movement, and as the introduction of better conductors makes it possible to transfer heat at the required rate with vanishing temperature differential, the ideal process develops as a limit which it is possible to approach. The reversible process is valuable in establishing a standard that cannot, even in theory, be exceeded.

**4:3. The Reversible Adiabatic Closed-system Process.** Since no heat flow is involved, reversibility can be conceived in an adiabatic process with less exercise of the imagination than is necessary for the other processes described in Chap. 2. It is also the type of change for which

the real process can be made to approach the ideal reversible process most closely for the same reason. The path followed by the reversible adiabatic is necessarily a maximum-work path (see Art. 2:12) over which  $dU/dV = -P/J$ . On pressure-volume coordinates this path would have, for any gas, somewhat the appearance of the path 1-2 in Fig. 4:1, which also shows the cylinder in which the expansion is pictured as taking place and the piston that forms a part of the external system which receives work during the expansion. The flywheel and connecting linkage

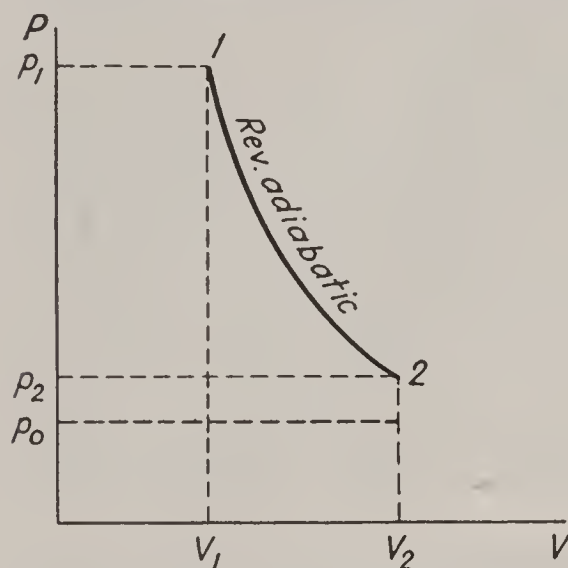
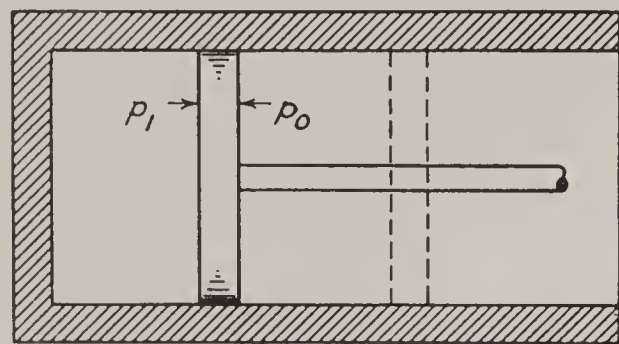


FIG. 4:1. The reversible adiabatic process.

are not shown. The walls and head of the cylinder are insulated to prevent the passage of heat. The piston, flywheel, and linkage are assumed frictionless, and the inertia of the flywheel is large so that only slow piston movement is attained in response to the force applied by the expanding system.

Our first assumption, for simplification, will be that the cylinder is located in a void so that all of the work delivered by the expanding gas system will be utilized in increasing the kinetic energy of the piston, flywheel, and linkage. Because of the slow piston movement that has been specified, the resistance offered by this external system is only infinitesimally less than the product of piston area and the pressure of the gas system against its stationary boundaries (the pressure plotted along

the path 1-2). As the piston moves from one dead-center position to the other, the work delivered to it is accordingly only infinitesimally less than the area under the path 1-2 on the  $PV$  diagram.

As the piston reaches the outer end of its stroke (point 2), the flywheel has its greatest store of kinetic energy. As the dead-center position is passed, the piston is moved back to the left at the expense of the stored energy of the flywheel until the force applied by the piston becomes infinitesimally greater than the resistance offered by the pressure of the gas system. Compression will then proceed over the system path 2-1 until the original state has been reached. The work required of the piston-flywheel external system during this return process is seen to be infinitesimally greater than that which it received during the expansion of the gas system, but this difference vanishes as the rate of piston movement decreases. Thus, as a limit, the flywheel will return to its original state



(which would include velocity as one of the properties) at the same time the gas system again reaches state 1. The process, as conceived and under the conditions that have been assumed, is declared to be reversible.

Now consider that the operation as described above did not take place in a void but in the midst of a vast medium having the pressure  $P_0$  and the temperature  $T_0$ . Since the gas system is thermally insulated, the temperature of the surroundings will have no effect upon its expansion or compression path. However, during expansion of the gas system a part of the work performed by this system must be expended in pushing the medium back against the resistance offered by its pressure as it acts against the rear face of the piston; this portion of the total work is represented by the area below the line  $P_0$  on the diagram and between the volume limits of the expansion. The balance of the work delivered by the gas system as it expands (the area above  $P_0$  and under the path 1-2) is all that is available for accelerating the piston-flywheel system, and the motion of the piston is thus slower than before. During the return stroke, this smaller storage of energy in the flywheel will none the less be sufficient to return the gas system to state 1, for on this stroke the medium will return work to that system equal to the amount received during the expansion. The process still conforms to our concept of reversibility, the only essential difference being that two external systems are involved instead of one.

**4:4. The Reversible Isothermal Process.** The simplest case that involves heat flow between the system and its surroundings develops when those surroundings remain at constant temperature during the process. This case is illustrated as it applies to a reversible process in Fig. 4:2. The walls of the cylinder are nonconducting as in Fig. 4:1, but the head is a perfect conductor of heat, and an external system  $S'$  that is capable of supplying or receiving heat without change of its temperature  $T_s$  is in contact with this head. Thus the temperature of the system enclosed within the cylinder and behind the piston may vary only infinitesimally from that of  $S'$ . A second external

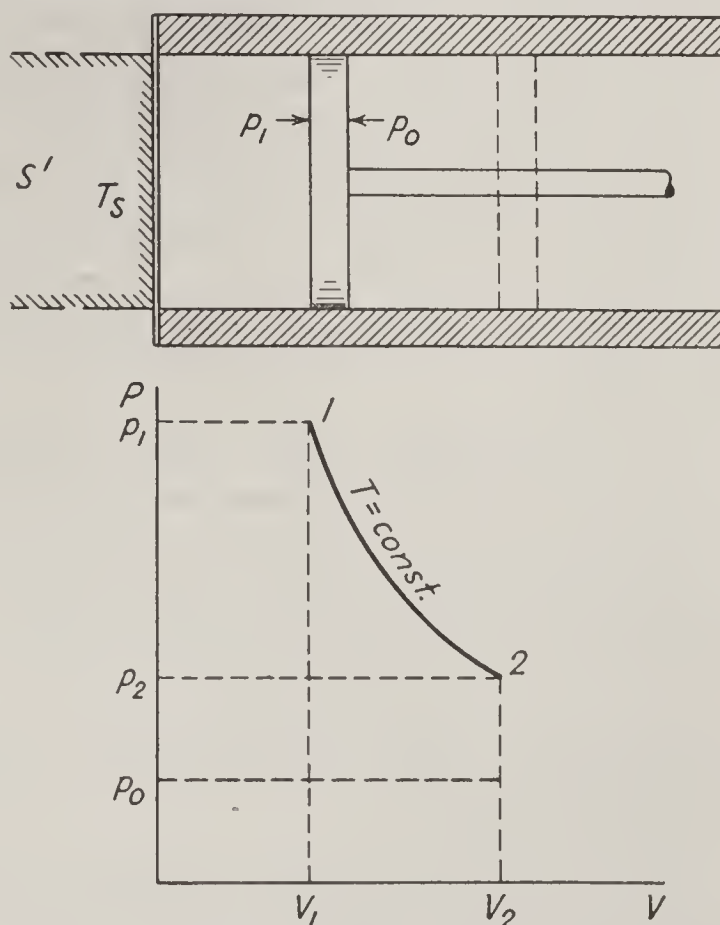


FIG. 4:2. The reversible isothermal process.

system  $S'$  that is capable of supplying or receiving heat without change of its temperature  $T_s$  is in contact with this head. Thus the temperature of the system enclosed within the cylinder and behind the piston may vary only infinitesimally from that of  $S'$ . A second external

system consisting of a frictionless piston-flywheel mechanism is provided to receive work and return it as before.

At the beginning of the process, the enclosed system has a state corresponding to state 1 on the pressure-volume diagram. The temperature  $T_1$  is identical with that of the external system  $S'$ . As the enclosed system undergoes the first infinitesimal stage of its expansion, there will be no flow of heat from  $S'$  until the temperature of the system has dropped infinitesimally below  $T_s$ . After that first step in the expansion, however, a flow of heat from  $S'$  will begin that will be sufficient to maintain the temperature of the enclosed system at  $T_s - dT$  and the path 1-2 will be an isothermal at this temperature level. As the process proceeds to its end point 2 (the end of the piston stroke), work is done on the piston-flywheel external system and the kinetic energy of that system is increased.

The direction of piston movement is now reversed, and the flywheel gives back some of its store of kinetic energy as the enclosed system is compressed. During the first infinitesimal stage of that compression the temperature of the enclosed system is raised to  $T_s + dT$ , after which it is maintained at this level as the system returns to state 1 over a path that is only infinitesimally above the path traced during the outward movement of the piston. As it retraces its path, the enclosed system may now, because of the favorable temperature differential which has been created, return to  $S'$  the same amount of heat that it received during the expansion. Neglecting differences of infinitesimal amount, both external systems have been returned to their original condition as the enclosed system reaches its original state, and the process may be classified as thermodynamically reversible.

**4:5. Reversible Heat Flow at Variable Temperature.** When the demonstration of a process requires both a flow of work across the boundaries of a system and the flow of heat across those boundaries while the temperature of the system changes finitely, the application of the concept of reversibility to that process becomes still more involved. The constant-pressure process illustrated in Fig. 4:3 is an example, though any variable-temperature path during which a change in system volume took place would also serve.

To conceive of this process as reversible requires the same cylinder with nonconducting walls and a head that is a perfect conductor of heat which was described in the preceding article. Instead of a single external system with which heat is exchanged, however, a series of such systems are placed in contact with the head of the cylinder, and the expansion of the enclosed system proceeds as a series of minute isothermals, the temperature at which each is carried out differing only infinitesimally from that of adjacent path segments. In retracing the process the external systems  $S'$  to  $S^n$  are brought into contact with the cylinder head in reverse order.



As the temperature differential between successive systems in the series  $S'$  to  $S^n$  decreases toward zero (and the number of individual systems in the series consequently increases toward infinity), the process will approach reversibility as a limit.

**4:6. The Constant-volume Reversible Process.** If the external system that supplies the heat necessary to demonstrate the constant-volume process, as described in Chap. 2, is at constant temperature, then that process is irreversible since the temperature of the enclosed system is not

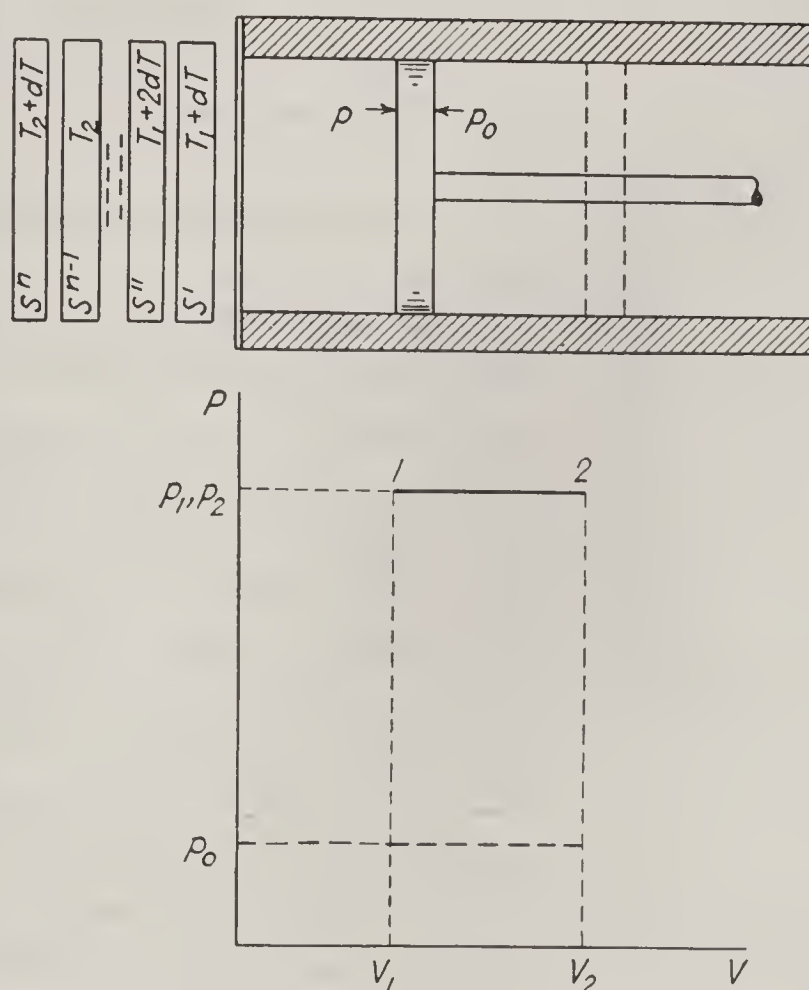


FIG. 4-3. The reversible constant-pressure process.

such that it can return this heat. If, however, a series of external systems is provided as suggested in the preceding article, the process may approach reversibility as a limit.

Consider the arrangement sketched in Fig. 4:4. The cylinder  $A$  is nonconducting and is fitted with a piston that is leakproof and is a part of a frictionless mechanism including a flywheel and the necessary linkage. A passage, the walls of which are also nonconducting, connects the opposite heads of the cylinder. This passage is divided into compartments separated by partitions that are nonconducting to heat but will permit the slow flow of fluid. Each compartment contains a capacitor that is capable of receiving and emitting heat; the reader may visualize these capacitors as consisting of metallic but porous material such as iron or copper filings. As we first examine the cylinder and passage, we find that the following observations apply:

1. The piston is at the bottom of the cylinder, and the air above it is at a uniform temperature  $T_1$ .

2. The capacitors vary in temperature from  $T_1 + dT$  to  $T_2 + dT$  from the top to the bottom of the passage, and each capacitor differs in temperature from adjacent capacitors by  $dT$ .

3. The thermal capacity of each capacitor is the same as that of the entire fluid system which is confined within the cylinder. That is, the

amount of heat that, when removed from the capacitor, will cause its temperature to decrease by  $dT$  will be sufficient to increase the temperature of the fluid system by  $dT$ .

4. The flywheel is assumed to be in slow motion.

Under the influence of the flywheel the piston will move upward in the cylinder. As it does so, the flywheel is not slowed, however, for the motion of the piston is so slow that the pressure on its upper and lower faces may be considered to differ only infinitesimally. When the piston has completed its upward stroke, the fluid will have been transferred to a location below it. As a result of heat received from the capacitors the temperature of the fluid is now  $T_2$ , and the temperature of each capacitor is lower than its original temperature by  $dT$ .

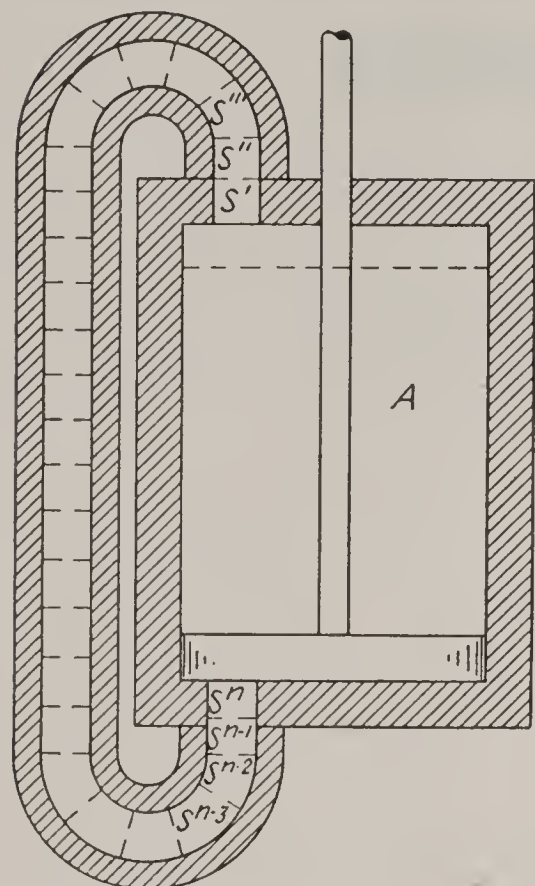


FIG. 4:4. The reversible constant-volume process.

As the piston begins its downward movement, the direction of fluid flow through the capacitors is reversed and, when the piston is again at the bottom of the cylinder, the temperature of the fluid will, neglecting differences of small order, be the same as it was originally; the same will be true of the temperatures of the capacitors. The motion of the flywheel has remained steady throughout, and the system of which it is a part has therefore returned to its original condition. No other systems have been affected.

The foregoing is an example of one method by which the constant-volume process may be conceived as taking place reversibly in the limit. This method will later have special interest to us since it illustrates how the *same amount of heat* that the system gave up as its temperature was reduced from a higher to a lower temperature might be made available for eventual return to the system with the purpose of increasing its temperature *between the same limits of temperature*. The reader will note that the



return of this heat would not be limited to cases in which the same path was followed in reverse but that it would also be available for return to the system over any constant-volume path that took place between the same temperature limits. Thus a proposed cycle may include two constant-volume processes that take place at different system volumes but for one of which the system temperature decreases from  $T_2$  to  $T_1$  while for the other the temperature increases from  $T_1$  to  $T_2$ . In that case the heat rejected during the first process may provide the heat supply during the second. In Eqs. (2:14) and (2:15) neither  $Q_s$  nor  $Q_R$  would include heat exchanged between the parts of the cycle in this manner, and reference to those equations will indicate that the efficiency of the cycle would be correspondingly increased. When processes are paired in this manner, the mutual exchange of heat is called *regeneration*. Regeneration may be applied between pairs of constant-pressure processes as well as those which take place at constant volume.

**4:7. External and Internal Reversibility.** The three factors any of which will always account for the irreversibility of a process have been shown to be friction, a finite pressure differential, and a finite temperature differential. In setting up the conditions under which each of the processes analyzed in the foregoing articles may approach reversibility, these factors are eliminated *at the boundaries of the system*. The processes may therefore be classified as *externally reversible*. If any of these factors operate *within* the boundaries of the system, the result is classified as *internal irreversibility*. If the system is not in equilibrium, a tendency will exist toward an internal change that will be irreversible in character.

For example, suppose the system to consist of two parts which differ finitely in temperature. The reader will realize that if these two parts are allowed to mix or even to exchange heat without intermingling, the operation is irreversible in the thermodynamic sense, for the system cannot be returned to its original state without calling on external systems for assistance and leaving a record in terms of the changed states of these external systems. The same will be true if the system is not in equilibrium by reason of a finite pressure differential between its parts and if this pressure difference is allowed to adjust itself within the system. Relative movement between two or more parts of the system which is accompanied by friction will also produce an internal irreversibility. The further stipulation as a condition for complete reversibility, external and internal, must therefore be made that *the path followed during any reversible process must connect equilibrium states of the system*.

Internal irreversibility may sometimes be eliminated by redefining the system in terms of new boundaries which will enclose only those parts of the original system which are in mutual equilibrium. All other parts thereafter are classified as external systems.

**4:8. Reversibility in Steady Flow.** A steady-flow process is reversible if the stream of fluid can be restored to its original state (including velocity and elevation as properties which assist in defining that state) by any means which will leave no history of the process in the changed states of external systems. An example is the steady adiabatic flow of a fluid through a frictionless nozzle and diffuser as illustrated in Fig. 4:5. During flow through the nozzle (from section 1 to section 2) the kinetic energy of the fluid increases by an amount equal to the decrease of enthalpy [see Eq. (3:11)]. In the diffuser (section 2 to section 3) exactly the opposite effect is caused, returning the stream to its original state without affecting any external system. This combination of nozzle and diffuser is called a venturi. In no real venturi will the increase of pressure between sections

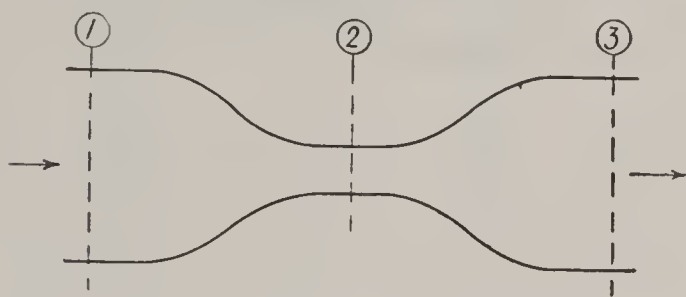


FIG. 4:5. Reversible steady flow.

2 and 3 be quite equal to the decrease that has taken place between sections 1 and 2. This reflects the effects of friction which enters into the picture in increased degree as the velocity mounts. The reversible process continues for steady flow to be a limiting process.

Irreversibility in steady flow is occasioned by the same three factors that apply in the closed-system process. When none of these is present, the process can be presumed to be reversible. Thus adiabatic flow through a turbine may be assumed to be reversible if the flow is frictionless and if no unrestrained expansion of the fluid has taken place, for the same work which was delivered by the turbine will be sufficient to return the stream of fluid to its original state through the agency of a frictionless compressor. No external system will have been affected. The path followed in both the turbine and the compressor will be that described in Art. 2:12.

*Example 4:8.* A gas having equations of state as in Example 1:10 enters a reversible adiabatic turbine at a pressure of 150 psig and a temperature of 1200°F. It is exhausted from the turbine at atmospheric pressure. (a) What is the exhaust temperature? (b) How much power does the turbine develop per pound of gas flow per second?

*Solution:*

$$(a) \quad p_1 = 150 + 14.7 = 164.7 \text{ psia}; \quad T_1 = 1200 + 460 = 1660^\circ\text{R}; \quad p_2 = 14.7 \text{ psia}; \\ k = 1.4 \text{ (see Example 2:12B)}; \quad v_1 = \frac{CT_1}{p_1} = \frac{(0.37)(1660)}{164.7} = 3.73 \text{ ft}^3/\text{lb}.$$

$$p_1 v_1^k = p_2 v_2^k \text{ or } v_2 = v_1 \left( \frac{p_1}{p_2} \right)^{1/k} = 3.73 \left( \frac{164.7}{14.7} \right)^{1/1.4} = (3.73)(5.63) = 21.0 \text{ ft}^3/\text{lb}$$

$$T_2 = \frac{p_2 v_2}{C} = (14.7)(21.0) = 833^\circ\text{R, or } 373^\circ\text{F}$$



$$(b) \ h_1 = 16 + 0.645p_1v_1 = 16 + (0.645)(164.7)(3.73) = 413 \text{ Btu/lb}$$

$$h_2 = 16 + (0.645)(14.7)(21.0) = 215 \text{ Btu/lb}$$

$${}_1W_2 = J(h_1 - h_2) = 778(413 - 215) = 154,000 \text{ ft-lb/lb} \quad [\text{Eq. (3:10)}]$$

The horsepower per pound of gas flow per second is  $154,000/550 = 280 \text{ hp}$ .

**4:9. The Carnot Engine.** By definition, the heat engine operates *continuously*. For continuous operation some sort of cycle of operations

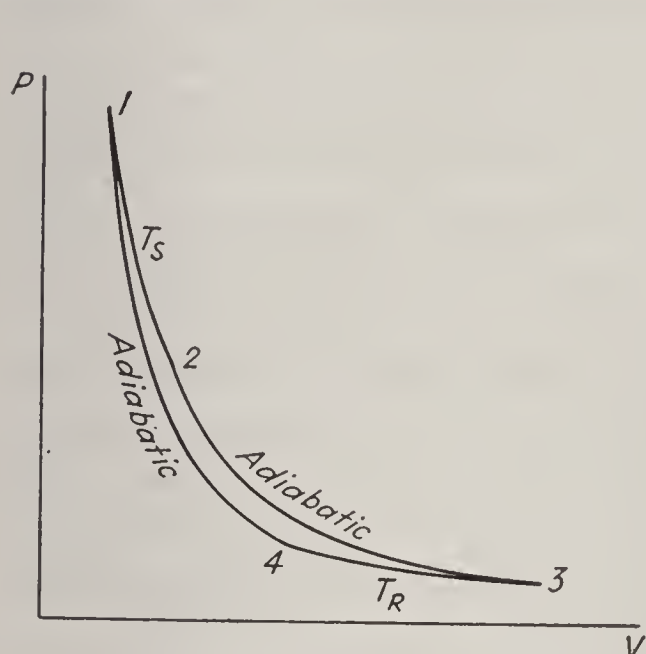


FIG. 4:6. The Carnot cycle (Example 4:8.)

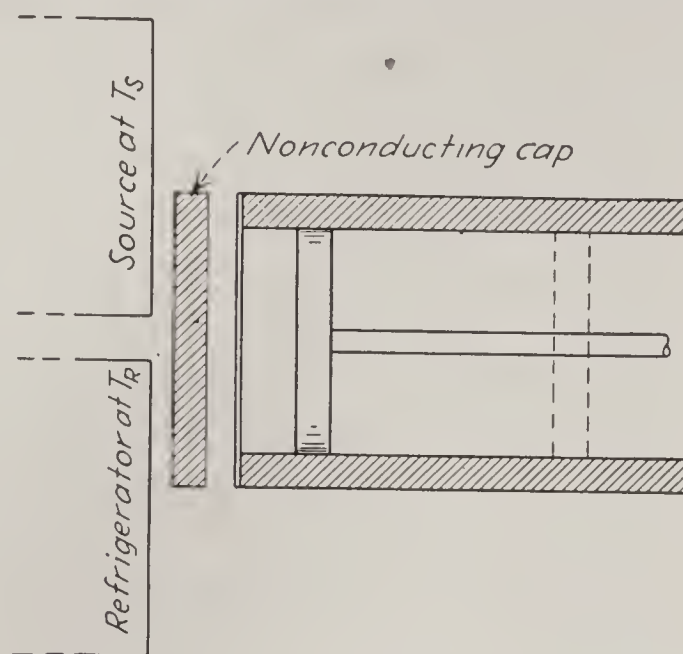


FIG. 4:7. The Carnot engine.

is required. It would seem probable that, for most effective performance of its function, the heat engine should operate on a cycle which consists exclusively of processes that are perfectly executed in the thermodynamic sense, *i.e.*, reversible. A cycle which is entirely composed of processes that are reversible is a *reversible cycle*.

In 1824 Sadi Carnot, a French scientist, proposed a reversible cycle during which heat would be exchanged only with a source at higher and a sink, or refrigerator, at lower temperature. His cycle, illustrated in Fig. 4:6 for a gas that has an equation of state similar to Eq. (1:6), consists of an isothermal expansion at the temperature  $T_S$  of the source and an isothermal compression at the lower temperature  $T_R$  of the refrigerator. These two isothermals are connected by two adiabatic processes, an adiabatic expansion which begins at the end of the isothermal expansion lowering the temperature of the system from  $T_S$  to  $T_R$  and an adiabatic compression that follows the isothermal compression and again raises the temperature of the system to  $T_S$ .

The Carnot engine operates on the cycle described above. A possible arrangement is diagramed in Fig. 4:7. A frictionless piston-flywheel system is provided as the agency for work delivery. The walls of the cylinder are nonconducting, but the head is a perfect conductor of heat. Provision is made for bringing instantaneously into contact with the head either the source at  $T_S$  or the refrigerator at  $T_R$ ; the head may also be

covered by a nonconducting cap. The first stage of the expansion is carried out with the source at  $T_s$  placed in contact with the head of the cylinder; the path 1-2, a reversible isothermal during which heat is received from the source at temperature  $T_s$ , results. When point 2 is reached, the source is instantaneously replaced by the nonconducting cap and the expansion continues to the end of the piston stroke; the path 2-3 is a reversible adiabatic during which the temperature of the system decreases to that of the refrigerator. At the instant that the piston reverses the direction of its motion (point 3 in the cycle) the refrigerator at  $T_R$  replaces the nonconducting cap. The first stage of the compression (3-4) therefore develops as a reversible isothermal compression at  $T_R$  during which heat is rejected to the refrigerator. The cycle is closed over path 4-1, which requires that, as the piston reaches point 4 of the cycle, the refrigerator is replaced by the nonconducting cap at the head of the cylinder and the rest of the stroke of the piston is carried out as a reversible adiabatic compression of the enclosed system. The only step then necessary to prepare for a retraversal of the cycle is to remove the nonconducting cap and move the source into position at the head of the cylinder.

Reviewing the characteristics of this engine and the cycle on which it operates it is noted that:

1. Heat is received only from a source at constant temperature and only during the process 1-2. To conform with the notation of Eqs. (2:14) and (2:15), the amount of heat transfer during this portion of the cycle may be designated as  $Q_s$ .

2. Heat is rejected only to a refrigerator at constant temperature and only during process 3-4. The amount of heat so transferred is  $Q_R$  [see Eq. (2:15)].

3. Since all processes are maximum-work processes, a net dividend of work, as represented by the area enclosed within the cycle, results from the traversal of the cycle. This amount of work must, by the First Law, equal  $Q_s - Q_R$ , and  $Q_s$  is therefore larger than  $Q_R$ .

4. Provision could be made for a lowered temperature  $T_R$  of the refrigerator with  $T_s$  unchanged by extending process 2-3 until this lower temperature was reached. This would also result in a lowering of the path 3-4 and a consequent increase in the enclosed area of the cycle and thus in the difference  $Q_s - Q_R$ . But process 1-2 need not be affected,  $Q_s$  would thus have the same value as before, and therefore  $Q_R$  must have decreased as  $T_R$  was reduced; the efficiency of the Carnot heat engine must have correspondingly increased [see Eqs. (2:14) and (2:15)].

5. Since all the processes which comprise the cycle on which its operation is based are individually reversible, the Carnot engine may follow them in reverse order (counterclockwise in Fig. 4:6 instead of clockwise).



In this case, as will be shown below, the Carnot *engine* will become a refrigerating machine, or *heat pump*.

In analyzing the action of the Carnot engine as a heat pump the term *hot body* will replace *source* in order to avoid confusion since it will develop that the high-temperature reservoir no longer supplies heat to the system but instead receives it from the system. The term *refrigerator* is still appropriate since it carries no implication of the direction of heat flow but does indicate that the temperature of that reservoir is relatively low.

In reversed traversal of the cycle we shall start, for convenience, at point 4 with the refrigerator at  $T_R$  in contact with the head of the cylinder. The process 4-3 is now an expansion during which the heat flow is the same in absolute amount, though opposite in direction, as for the process 3-4 in clockwise movement around the cycle. At point 3 the nonconducting cap replaces the refrigerator, and, during the reversible adiabatic compression 3-2, the temperature of the system rises to that of the hot body ( $T_S$ ). At point 2 the nonconducting cap is removed, the hot body placed in position, and an isothermal compression 2-1 at  $T_S$  thereafter proceeds. Evidently the heat transfer for this process is the same in amount ( $Q_S$ ) as for process 1-2 though now the heat flows from the system into the hot body. When point 1 is reached, the nonconducting cap is again placed in position and the cycle is closed by the reversible adiabatic process 1-4.

Comparing the operation of the Carnot heat engine with that of the Carnot heat pump which operates on the same cycle but in the reverse direction, it is seen that neither the amount of heat exchange with each of these reservoirs nor the net work exchanged with other external systems has changed; the *direction* of energy flow alone differs. The term reversible engine thus assumes a greater significance than simply that of an engine that operates on a cycle composed entirely of reversible processes. For a reversible engine, after operation for a period as an engine, could be reversed to travel its cycle in the opposite direction (as a heat pump) and would be capable of restoring to its source all of the heat that it had received from that source, at the expense only of heat taken from the refrigerator which had, during operation as an engine, been deposited with that refrigerator, and of work returned by other systems with which it had been deposited. Thus the engine is reversible in the sense that it can restore all systems to their original states and leave no history of its operation on them.

There are no real Carnot engines. A review of the conditions that surround the operation of such devices will be sufficient indication to the reader as to why they are not practical devices. Their absence from the real power plant does not change the value of the Carnot-engine concept as a device which serves as the basis of interesting speculation in the field of thermodynamics.

The Carnot engine has in this article been described and analyzed in its classic form, with respect to its operation on a closed-system cycle. With suitable changes in apparatus and the introduction of flow around a closed circuit, an equivalent open-system cycle could be devised; for the present, this is left to the reader to demonstrate.

*Example 4:9.* The system contained within a Carnot engine (the working substance) consists of 1 lb of the gas for which equations of state are as in Example 1:10. Referring to the notation of Fig. 4:6,  $V_1 = 3 \text{ ft}^3$ ,  $V_2 = 6 \text{ ft}^3$ ,  $t_S = 500^\circ\text{F}$ , and  $t_R = 100^\circ\text{F}$ . (a) Calculate the pressure, volume, and temperature at points 1, 2, 3, and 4 around the cycle. (b) Calculate  $Q_S$  and  $Q_R$  per cycle and, by difference, the net work of the cycle. (c) Calculate the work which accompanies each of the processes, and obtain the net work of the cycle as the total. (d) Compare the net work of the cycle with the gross work of expansion (the sum of the work performed during processes 1-2 and 2-3). (e) What is the efficiency of the cycle?

*Solution:*

$$(a) \text{ Point 1: } v_1 = V_1 = 3 \text{ ft}^3; T_1 = T_S = 960^\circ\text{R}; p_1 = \frac{CT_1}{v_1} = \frac{(0.37)(960)}{3} = 118.5 \text{ psia}$$

$$\text{Point 2: } v_2 = V_2 = 6 \text{ ft}^3; T_2 = T_S = 960^\circ\text{R}; p_2 = \frac{CT_2}{v_2} = \frac{(0.37)(960)}{6} = 59.25 \text{ psia}$$

$$\text{Point 3: } T_3 = T_R = 560^\circ\text{R}; \frac{p_2 v_2}{p_3 v_3} = \frac{T_2}{T_3} \text{ or } \frac{p_2}{p_3} = \frac{v_3}{v_2} \frac{T_2}{T_3} \quad [\text{Eq. (1:6)}]$$

$$p_2 v_2^k = p_3 v_3^k \text{ or } \frac{p_2}{p_3} = \left( \frac{v_3}{v_2} \right)^k \quad [\text{Ex. 2:12A}]$$

Equating these values of  $p_2/p_3$

$$\left( \frac{v_3}{v_2} \right)^k = \left( \frac{v_3}{v_2} \right) \left( \frac{T_2}{T_3} \right) \text{ or } \left( \frac{v_3}{v_2} \right)^{k-1} = \frac{T_2}{T_3} \text{ and } \frac{v_3}{v_2} = \left( \frac{T_2}{T_3} \right)^{1/(k-1)}$$

Thus, since  $k = 1.4$  (from Example 2:12B),

$$v_3 = v_2 \left( \frac{T_2}{T_3} \right)^{1/(k-1)} = 6 \left( \frac{960}{560} \right)^{1/(1.4-1)} = (6)(1.713)^{2.5} = (6)(3.85) = 23.1 \text{ ft}^3$$

$$p_3 = \frac{CT_3}{v_3} = \frac{(0.37)(560)}{23.1} = 8.98 \text{ psia}$$

Point 4:  $T_4 = T_R = 560^\circ\text{R}$

$$v_4 = v_1 \left( \frac{T_1}{T_4} \right)^{1/(k-1)} = 3 \left( \frac{960}{560} \right)^{1/(1.4-1)} = (3)(3.85) = 11.55 \text{ ft}^3$$

$$p_4 = \frac{(0.37)(560)}{11.55} = 17.96 \text{ psia}$$

$$(b) \begin{aligned} u_1 &= 16 + (0.46)(118.5)(3) = 179.5 \text{ Btu}; u_2 = 16 + (0.46)(59.25)(6) = 179.5 \text{ Btu} \\ u_3 &= 16 + (0.46)(8.98)(23.1) = 111.5 \text{ Btu}; u_4 = 16 + (0.46)(17.96)(11.55) \\ &= 111.5 \text{ Btu} \end{aligned}$$

$$Q_S = u_2 - u_1 + {}_1W_2/J = 179.5 - 179.5 + {}_1W_2/J = {}_1W_2/J$$

For the isothermal processes 1-2 and 3-4,  $pv = \text{const} = CT$  or  $P = 144CT/v$ .

$$\begin{aligned} {}_1W_2 &= \int_{V_1}^{V_2} P dV = 144CT_S \int_{V_1}^{V_2} \frac{dv}{v} = 144CT_S \log_e \frac{v_2}{v_1} \\ &= (144)(0.37)(960) \log_e \frac{6}{3} = (51,100)(0.693) = 35,400 \text{ ft-lb} \\ Q_S &= {}_1W_2/J = 35,400/778 = 45.5 \text{ Btu} \end{aligned}$$



Similarly,

$$\begin{aligned} {}_3W_4 &= \int_{V_3}^{V_4} P dV = 144CT_R \int_{v_3}^{v_4} \frac{dv}{v} = 144CT_R \log_e \frac{v_4}{v_3} = (144)(0.37)(560) \log_e \frac{11.55}{23.1} \\ &= (29,800)(-0.693) = -20,650 \text{ ft-lb} \end{aligned}$$

$$Q_R = -\frac{{}_3W_4}{J} = -\frac{-20,650}{778} = 26.5 \text{ Btu}$$

$$\text{Net work of cycle} = J(Q_S - Q_R) = 778(45.5 - 26.5) = 14,750 \text{ ft-lb or 19 Btu}$$

$$(c) {}_1W_2 = 35,400 \text{ ft-lb}; {}_2W_3 = J(u_2 - u_3) = 778(179.5 - 111.5) = 52,900 \text{ ft-lb}$$

$${}_3W_4 = -20,650 \text{ ft-lb}; {}_4W_1 = J(u_4 - u_1) = 778(111.5 - 179.5) = -52,900 \text{ ft-lb}$$

$$\begin{aligned} \text{Net work of cycle} &= {}_1W_2 + {}_2W_3 + {}_3W_4 + {}_4W_1 \\ &= 35,400 + 52,900 - 20,650 - 52,900 = 14,750 \text{ ft-lb} \end{aligned}$$

$$(d) \text{ Ratio of net work of cycle to gross work of expansion} = \frac{14,750}{35,400 + 52,900} = 0.167$$

The low value of this ratio makes clear one of the reasons why the Carnot cycle is not a satisfactory cycle on which to base the operation of a real engine. The effects of friction on the real engine might be expected to be of such magnitude as to decrease the work of expansion by about 10 per cent and to increase the work of compression in about the same proportion. Applying this proportion to the example, the work of expansion would be  $0.9(35,400 + 52,900) = 79,500 \text{ ft-lb}$  and the work of compression  $1.1(-20,650 - 52,900) = -81,000 \text{ ft-lb}$ . Thus the real engine, instead of supplying work to other systems, would require work from those other systems to help in overcoming frictional effects.

(e) The efficiency of the *reversible Carnot engine* is, for the conditions of this example,

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{45.5 - 26.5}{45.5} = 0.417$$

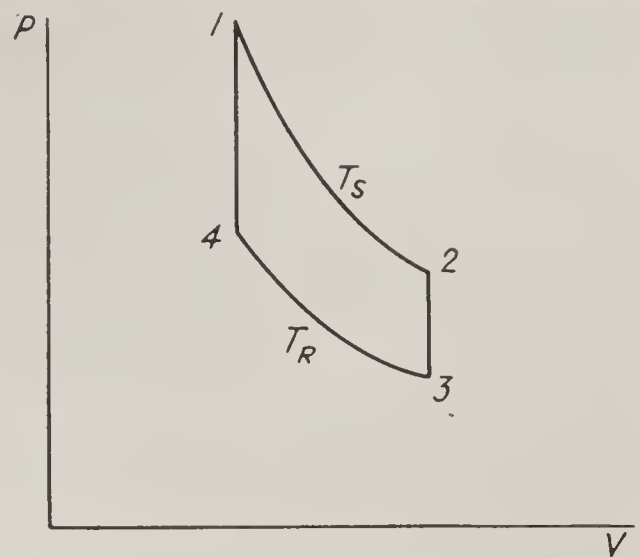


FIG. 4:8. The Stirling cycle.

**4:10. The Stirling Cycle and Stirling Engine.** Many reversible cycles will suggest themselves to the reader; all that is necessary is to set up any combination of individually reversible processes that will eventually return the system to its original state. A few of these cycles may also have the important characteristic of the Carnot cycle in that they exchange heat only with two external reservoirs, each of which is at constant temperature. An example of this is the Stirling cycle.

The Stirling cycle is illustrated in Fig. 4:8. It consists of an isothermal 1-2 at the constant temperature  $T_S$  of the source and an isothermal 3-4 at the constant temperature  $T_R$  of the refrigerator. These are connected by the constant-volume processes 2-3 and 4-1. During the process 2-3 the temperature of the working system drops from  $T_S$  to  $T_R$  and, during 4-1, increases again from  $T_R$  to  $T_S$ . Since these two processes take place over the same temperature range, even though at different system volumes,

regeneration, as described in Art. 4:6, may be employed and the heat that is discharged by the system during the process represented by the path 2-3 may be restored to the system during process 4-1. These heat amounts would then not be included in  $Q_R$  or  $Q_S$ . This is equivalent to making the capacitors described in Art. 4:6 a part of the system.

The operation of the Stirling engine is based on the Stirling cycle as described above. It is similar to the Carnot engine in that it is reversible, with all which that implies, when the source from which it draws heat and the refrigerator to which heat is discharged are at, respectively, constant temperature. It is dissimilar in the relative complexity of the apparatus which is required to carry out the necessary operations. Yet real Stirling engines are built and operated. These are not reversible engines, of course, and their efficiency falls far below that which we shall later calculate as applying to the reversible engine. The point of principal interest about the Stirling engine is that, as a reversible engine, it furnishes a basis of comparison with the reversible Carnot engine under equivalent conditions of operation, *viz.*, constant temperature of source and constant refrigerator temperature.

The features of the design of the Stirling engine that enable it to operate on the Stirling cycle will be discussed at a later and more appropriate stage in our discussion. For the present it need only be said that the Stirling engine requires two pistons, a working piston and a displacer piston. The former moves during the isothermal processes, the latter as regeneration is employed to accompany the constant-volume processes.

*Example 4:10.* The system contained within a Stirling engine consists of 1 lb of the gas for which equations of state are as in Example 1:10. Referring to the notation of Fig. 4:8,  $V_1 = 3 \text{ ft}^3$ ,  $V_2 = 6 \text{ ft}^3$ ,  $t_S = 500^\circ\text{F}$ , and  $t_R = 100^\circ\text{F}$ . (a) Calculate the pressure, volume, and temperature at points 1, 2, 3, and 4 around the cycle. (b) Calculate the heat rejected to the regenerator ( ${}_2Q_3$ ) and restored to the cycle during process 4-1. (c) Calculate  $Q_S$  and  $Q_R$  per cycle and, by difference, the net work of the cycle. (d) Compare the net work of the cycle with the gross work of expansion. (e) What is the efficiency of the reversible engine?

*Solution:*

$$(a) \text{ Point 1: } T_1 = T_S = 960^\circ\text{R}; v_1 = V_1 = 3 \text{ ft}^3; p_1 = \frac{CT_1}{v_1} = \frac{(0.37)(960)}{3} = 118.5 \text{ psia}$$

$$\text{Point 2: } T_2 = T_S = 960^\circ\text{R}; v_2 = V_2 = 6 \text{ ft}^3; p_2 = 59.25 \text{ psia}$$

$$\text{Point 3: } T_3 = T_R = 560^\circ\text{R}; v_3 = v_2 = 6 \text{ ft}^3; p_3 = \frac{CT_3}{v_3} = \frac{(0.37)(560)}{6} = 34.5 \text{ psia}$$

$$\text{Point 4: } T_4 = T_R = 560^\circ\text{R}; v_4 = v_1 = 3 \text{ ft}^3; p_4 = \frac{CT_4}{v_4} = 69.0 \text{ psia}$$

$$(b) u_1 = u_2 = 179.5 \text{ Btu}$$

[Ex. 4:9]

$$u_3 = 16 + (0.46)(34.5)(6) = 111.5 \text{ Btu}; u_4 = 16 + (0.46)(69)(3) = 111.5 \text{ Btu}$$

$$\text{Heat rejected to regenerator} = -{}_2Q_3 = -(u_3 - u_2) = -(111.5 - 179.5) = 68 \text{ Btu}$$

$$\text{Heat restored from regenerator} = {}_4Q_1 = u_1 - u_4 = 179.5 - 111.5 = 68 \text{ Btu}$$



$$\begin{aligned}
 (c) \quad Q_S &= \frac{{}_1W_2}{J} = 45.5 \text{ Btu}; \quad Q_R = -\frac{{}_3W_4}{J} = -\frac{144CT}{J} R \log_e \frac{v_4}{v_3} \\
 &= -\frac{(144)(0.37)(560)}{778} \log_e \frac{3}{6} \\
 &= -(38.3)(-0.693) = 26.5 \text{ Btu}
 \end{aligned}$$

$$\text{Net work of cycle} = J(Q_S - Q_R) = 778(45.5 - 26.5) = 14,750 \text{ ft-lb or } 19 \text{ Btu}$$

(d) Ratio of net work of cycle to gross work of expansion =  $14,750/{}_1W_2 = 14,750/(778)(45.5) = 0.417$ . The higher value of this ratio as compared with the corresponding ratio for the equivalent Carnot cycle indicates that the real engine to operate on the Stirling cycle would not be handicapped in the same degree as the real Carnot engine. For instance, if we apply the assumptions of Example 4:9, the work of expansion for this real Stirling engine would be  $(0.9)(778)(45.5) = 31,800 \text{ ft-lb}$  and the work of compression  $(1.1)(778)(-26.5) = -22,700 \text{ ft-lb}$ , leaving a net dividend of 9100 ft-lb of useful work. On the other hand, the introduction of regeneration into the Stirling-engine cycle causes additional irreversibilities in the operation of the real Stirling engine with which the real Carnot engine would not have to contend.

(e) The efficiency of the *reversible Stirling engine* is, for the conditions of this example,

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{45.5 - 26.5}{45.5} = 0.417$$

It will be observed that this is the same efficiency that was calculated to apply to the reversible Carnot engine which operated under equivalent conditions as to the temperatures of source and refrigerator.

### Problems

1. Show that, in reversible adiabatic steady flow through an open system, the relation between the pressure and the specific volume of an ideal gas may be expressed as  $Pv^k = \text{const}$ . [Hint: Consider that a unit weight of the gas constitutes a second system (a closed system) with which the observer travels as it moves through the open system.]

2. Work Example 4:8, assuming the gas is (a) gas *W*; (b) gas *X*; (c) gas *Z*.

3. In solving Example 4:8, what assumption was made with respect to the velocities at entrance to and exit from the open system contained within the turbine? If these velocities had been, respectively, 100 and 500 fps, how would the answers have been changed, if at all?

4. A gas at 1200°F moves steadily through a reversible isothermal turbine. The pressure at entrance is 150 psig, and the exhaust is to atmospheric pressure. Assume that the velocities and elevations at entrance and exit are equal. If the gas is (a) gas *W*, (b) gas *X*, (c) gas *Y*, (d) gas *Z*, calculate the work delivered to the turbine shaft and the rate of heat flow into the turbine per pound of gas flow. (Hint: The amount of work delivered to the turbine shaft per pound of gas flow is equal to the amount of work observed to accompany the expansion of a 1-lb closed system as it moves through the turbine by an observer who travels with the system minus the net flow work,  $P_1v_1 - P_2v_2$ , which is expended in the course of entering and leaving the turbine rather than in turning the shaft.)

5. Work Example 4:9, assuming the system consists of 1 lb of (a) gas *W*; (b) gas *X*; (c) gas *Z*. Compare your answers with those obtained in the solution of the example for gas *Y*, and note any similarities.

6. (a) Work Example 4:9, changing  $t_s$  to 1000°F. Repeat this solution using (b) gas *W*; (c) gas *X*; (d) gas *Z*. What effect does this change have on the cycle efficiency?

7. (a) Work Example 4:9, changing  $t_R$  to 200°F. Repeat this solution, using (b) gas  $W$ ; (c) gas  $X$ ; (d) gas  $Z$ . Discuss the effect of this change on the cycle efficiency.

8. Work Example 4:10, assuming that the system consists of 1 lb of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ . Compare your answers with those of the example, and state whether or not each gas is to be preferred to gas  $Y$  and why.

9. Work Example 4:10, changing  $t_S$  to 1000°F.

10. Work Example 4:10, changing  $t_R$  to 200°F.

11. If regeneration is not employed in the Stirling cycle of Example 4:10 but the state path is the same and all processes are maximum-work (reversible) processes, what is the efficiency of the cycle? How does the average temperature at which heat was received from the source compare for this cycle with the original (Stirling) cycle? What is the effect on the average temperature at which heat is rejected to the refrigerator?

12. A reversible cycle encloses an area of 3.5 in.<sup>2</sup> when plotted on a  $pV$  diagram on which 1 in. denotes a pressure differential of 80 psi and a volume change of 0.5 ft<sup>3</sup>. When traversed clockwise, 50 Btu is rejected to the refrigerator for each traversal of the cycle. What is the cycle efficiency?

13. Are the following processes reversible or irreversible? Neglect heat flow except as specifically stated to take place. If a process is reversible, show how all systems may be returned to their original states. If irreversible, classify the irreversibility as to cause or causes.

(a) A weight slides frictionlessly down an inclined plane.

(b) A weight slides down a rough inclined plane; it is slowed by friction.

(c) A perfectly elastic spring is elongated.

(d) A marble drops from the rim of a bowl and eventually comes to rest at the bottom of the bowl.

(e) A fluid expands slowly behind a frictionless piston in an insulated cylinder.

(f) Water is confined under a piston which exerts a constant pressure on its surface; the temperature of the water is raised by stirring.

(g) The process outlined in (f) continues until the water evaporates.

(h) Water confined as in (f) increases in temperature as the result of heat received from a source at constant temperature.

(i) A perfectly elastic ball is dropped through a void, striking a rigid floor.

(j) The ball of (i) drops through the air.

(k) A gas is confined in an insulated cylinder beneath a weighted piston which is supported on a stop. The stop is removed and the piston drops suddenly until the pressure of the gas becomes sufficient to support its weight.

(l) Steam flows through a frictionless nozzle, decreasing in pressure and increasing in velocity.

(m) Steam flows through a small orifice from a chamber at high pressure to a chamber at considerably lower pressure. Eddies are formed below the orifice which are gradually damped out.

(n) The steam jet leaving the nozzle in (l) is expelled into a large chamber in which eddies are formed and which it leaves at low velocity.

(o) A stream of water at 80°F is mixed with a stream of steam at 212°F. The steam is condensed and the mixture leaves at 200°F.

14. Each of the following processes is irreversible. With respect to the systems defined by the italicized words, state whether the irreversibility is external or internal. When internal, can you define a boundary which will separate the system into two systems which remain distinct from each other and for at least one of which there is no internal irreversibility?



(a) A closed rigid container with insulated walls contains a *gas* and an *electrical heating element* to which current is supplied from a source external to the container. The temperature and pressure of the gas increase.

(b) A *gas* is confined within a cylinder with nonconducting walls and head. The gas is compressed by the rapid inward movement of a frictionless piston.

(c) A rigid container is divided into two compartments by a rigid partition. One compartment contains *gas W* at pressure  $P$  and temperature  $T$ ; the other contains *gas X* at pressure  $\frac{1}{2}P$  and temperature  $T$ . An opening is made in the partition and the two gases mix.

(d) Same as (c) except that the pressures are equal but the original temperatures differ.

(e) Same as (c) except that both the temperatures and the pressures are equal in the two compartments before the partition is ruptured.

(f) A *copper ball* at  $50^{\circ}\text{F}$  is placed in a pail of *water* at  $120^{\circ}\text{F}$ . The ball and the water reach a common temperature.

(g) A *closed rigid container filled with a gas* is immersed in a bath of hot water. The temperature of the container and its contents rises.

(h) *Two gallons of water* at  $100^{\circ}\text{F}$  are mixed with *1 gal of water* at  $70^{\circ}\text{F}$ . A common temperature is reached.

(i) A *stream of steam* flows through a reducing valve, decreasing in pressure but doing no external work. Downstream from the valve the elevation and the velocity are the same as upstream.

Symbols

$C$	constant
$h$	specific enthalpy
$J$	proportionality factor
$k$	a constant ratio
$p$	pressure, psi
$P$	pressure; pressure, psf
$Q$	heat flow; rate of heat flow
$T$	absolute temperature
$u$	specific internal energy
$U$	internal energy of a system
$v$	specific volume
$V$	volume of a system
$W$	work

Greek Letters

$\eta$	efficiency of a heat engine
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Subscripts

$R$	refrigerator
$S$	source

## CHAPTER 5

### THE SECOND LAW OF THERMODYNAMICS

**5:1. Inadequacy of the First Law.** The First Law states that when energy in one form disappears energy in another form must make its appearance in equivalent amount. It does not attempt to establish conditions under which such energy transfers may take place or to limit the extent to which conversion may be effected. Thus, as based on the First Law, the work that would result from the adiabatic expansion of a closed system was shown to be equal to the decrease of internal energy of the system. No limit was set upon the amount of that decrease until we went beyond the scope of the First Law to specify that *if the process was a maximum-work process* the rate of change of internal energy with respect to system volume would equal the negative pressure. We were then, although not informed of it at the time, in the realm of the Second Law.

Many other instances may be cited of observations that transcend the implications of the First Law. The elementary observation, for example, that the direction of spontaneous heat flow is always toward the system at lower temperature is an encroachment on Second Law territory. The whole concept of reversibility of which we treated in the last chapter is based on Second Law principles. A statement of the Second Law and an examination of its implications can no longer be delayed.

**5:2. The Second Law.** Formal statements of the Second Law are based on observations of its operation. The observations that may be made are many and various as has been indicated above, and it is not surprising to find that a multitude of statements are proposed to express the meaning of the law. One of the earliest and simplest was offered by Rudolf Clausius, a nineteenth-century scientist; it follows:

*Heat cannot, of itself, pass from a colder to a hotter system.* A second statement, credited to Planck,<sup>1</sup> is as follows:

*It is impossible to construct an engine that will work in a complete cycle and produce no effect except to raise a weight and exchange heat with a single reservoir.*

Planck's version of the Second Law is well adapted to the purposes of engineering thermodynamics, and our later references to the Second Law will in general be based on his statement.

<sup>1</sup> Max Planck, "Treatise on Thermodynamics," Longmans, Green & Co., New York, 1927.



The two statements of the Second Law that are presented above are equivalent each to the other, for it may be shown that Planck's statement, if false, will cause the Second Law as stated by Clausius also to be false. Assume, contrary to Planck's statement, that a machine is available that will continuously change the heat received from a single reservoir into work. By the First Law this conversion must be complete, and all of the heat received will be converted into work. As illustrated in Fig. 5:1, the work delivered by this machine ( $P$ ) will be used to operate a Carnot heat pump ( $C$ ) which will draw  $Q_R$  heat units per unit of time from a low-temperature refrigerator and will discharge  $Q_S$  heat units (larger than  $Q_R$  by the amount of work required to drive the Carnot heat pump) to the reservoir at higher temperature  $T_S$  that is the source of heat supply for  $P$ . This reservoir need supply only  $Q_S - Q_R$  heat units to  $P$  while it receives  $Q_S$  heat units from  $C$ . The Second Law, as stated by Clausius, has been proved false if Planck's statement is not true since no systems except the reservoirs at  $T_R$  and  $T_S$  have been affected and heat has passed from the one at lower to the one at higher temperature.

The Second Law, like the First Law, may be proved only by the failure of all attempts to disprove it. If it were not true, all worry as to the continued availability of fuels as a source of heat and power would vanish, for it would be possible to tap the limitless stores of energy in the seas and the atmosphere for this purpose. In Fig. 5:1, if the rate at which engine  $P$  receives heat is increased to  $Q_S$  units per unit of time, that engine will provide a surplus of power equal to  $Q_R$ . In this case the high-temperature reservoir has given only as much heat as

it received from the Carnot heat pump and may be replaced by a conductor. No violation of the First Law has occurred since the work delivery was at the rate at which energy in the form of heat was supplied by the refrigerator. But the net work output is at the expense of the thermal energy of one reservoir only, and the Second Law is violated.

Not only would fuel be saved, but there would be an additional gain of no small importance when a need existed to create a temperature below that of surrounding systems. For the space to be cooled could provide a source of heat and thereby have its temperature lowered. To provide a graphic example and carry this idea to its ultimate of absurdity, our homes could be air-conditioned in hot weather not only without expense for

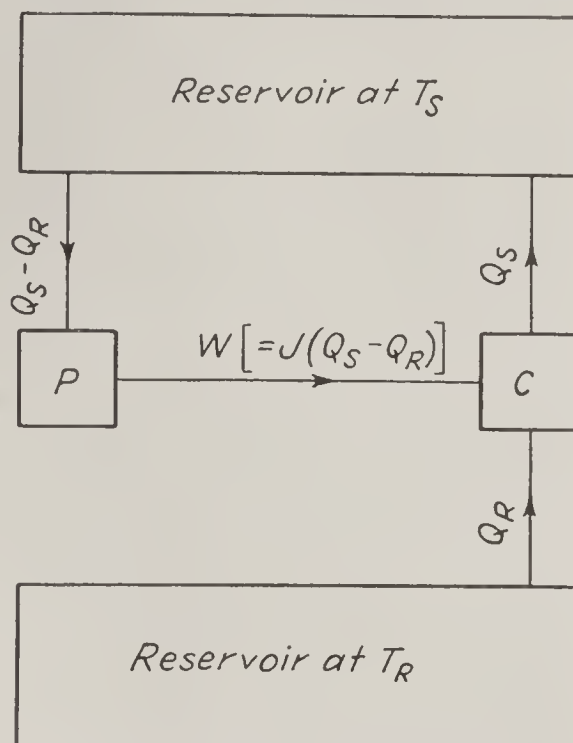


FIG. 5:1. The Second Law.

power but even with a net dividend of power that could be used to operate the vacuum cleaner and the toaster. This example illustrates why a machine of this kind is often called a perpetual-motion machine *of the second kind*. The first class of perpetual-motion machine is a contradiction of the First Law since these machines are designed to create energy. This second class of perpetual-motion machine involves no violation of the First Law, as has been shown, but the idea behind it is just as absurd from a thermodynamic standpoint. The Second Law may be said to deny the feasibility of a perpetual-motion machine of the second kind.

**5:3. Reversibility and the Second Law.** It is of interest to apply Planck's statement of the Second Law to the concept of reversibility that was introduced in Chap. 4. In the course of that discussion we arrived at the conclusion that friction, unrestrained expansion, or the flow of heat across a finite temperature interval would always cause irreversibility in a process. It will be shown that if a process which involved any of these effects were reversible a machine of the type declared impossible by the Second Law would be a possible result.

In Chap. 4 it has been reasoned that maximum work is associated with the reversible process. Let us first show that this reasoning is in accord with the Second Law. We shall assume that a process may be found which, with the system in communication with a single reservoir only, will deliver more work than a reversible process that takes place with the system in communication only with the same reservoir and that connects the same two end states. By definition of reversibility, a third process must also be possible which is the reverse of the reversible process and which will return the system to its original state, affecting only the single reservoir and requiring from that reservoir only the same amount of work that was transferred from it during the reversible process. But this amount of work is less than that delivered by the system during the assumed process, and a cycle may be formed of the assumed process and this third process for which  $\oint \partial W > 0$ . Since the system was in communication with only a single reservoir, a contradiction of Second Law principles is observed and the assumption must be abandoned.

It has been shown in Chap. 2 that friction and unrestrained expansion cause the work associated with the tracing of a given state path to be less than the maximum. Their presence during any process must, according to the preceding paragraph, make that process irreversible.

It remains only to show that the flow of heat across a finite temperature interval is irreversible. Heat may flow from a reservoir at higher to a system at lower temperature without affecting other systems. But the possibility of heat flow in the opposite direction without affecting other systems is directly denied by Clausius' statement of the Second Law, and his statement has been shown to be the equivalent of that of Planck.



**5:4. The Second Law and the Carnot Engine.** Even a cursory examination of the Second Law will indicate that one of its important implications is to the effect that, for the continuous conversion of heat into work (power), a minimum of two reservoirs must be available. A Carnot engine is a device that could be employed for the purpose. In order that the operation of the Carnot engine may return a net dividend of power, it is required that its source and its refrigerator shall differ in their temperatures. Thus it is seen that the characteristic in which the two reservoirs required by the Second Law must differ is their temperature.

Further, it has been shown that the heat discharged by a Carnot engine to its refrigerator will decrease with respect to a given amount of heat which it receives from a source at fixed temperature as the temperature of the refrigerator is lowered (see Art. 4:9) and that the net dividend of work that it delivers will correspondingly increase. Since this dividend of work can only equal the difference,  $Q_S - Q_R$ , between the heat received from the source and that rejected to the refrigerator, the implication of the Second Law that not all of the energy received as heat from the source can be continuously converted into work is sustained.

The Carnot engine is shortly to become our tool for evaluating the effects of the operation of the Second Law on a quantitative basis. Before it can be used for that purpose, it becomes necessary to prove that its performance cannot be exceeded by that of any other engine which operates under equivalent conditions.

**5:5. The Carnot Principle.** The Carnot engine derives its importance not because of its practical utility but because it is an example of a reversible engine. It was devised by Carnot to accompany the statement of a principle of great importance in thermodynamics:

*No engine working continuously between given fixed and uniform temperatures of source and refrigerator can have a greater efficiency than a reversible engine that operates between these same reservoirs.*

The proof of the Carnot principle is based on the Second Law. Let it be assumed that the principle is not valid and that an engine may accordingly be constructed which, when operating between a given source and a given refrigerator, will have an efficiency higher than that of a Carnot (reversible) engine which operates between the same reservoirs. Both engines will be placed between source and refrigerator as shown in Fig. 5:2. When operated as engines so that each withdraws heat from the source at a rate (per unit of time) which will be designated as  $Q_S$ , the Carnot engine  $C$  will reject  $Q_R$  units of heat and the irreversible engine  $I$  will discharge  $Q_A$  units of heat to the refrigerator in the same time interval. By assumption the efficiency of engine  $I$  exceeds that of  $C$ , and therefore  $Q_R > Q_A$ .

The Carnot engine  $C$  is reversible and therefore can and will be reversed.

As a heat pump it will receive  $Q_R$  units of heat from the refrigerator, discharge  $Q_S$  units to the source, and require that work be supplied at the rate  $Q_S - Q_R$  to drive it. The work output of engine  $I$  is  $Q_S - Q_A$ , and this will be more than sufficient to operate engine  $C$ ; a work dividend available for other purposes and equal to  $Q_R - Q_A$  will result. Examination indicates that the source at  $T_S$  may be replaced by a conductor (since it gives and receives heat at the same rate) and that the work dividend  $Q_R - Q_A$  is solely at the expense of an equivalent amount of energy removed as heat from the refrigerator. This is a violation of the Second

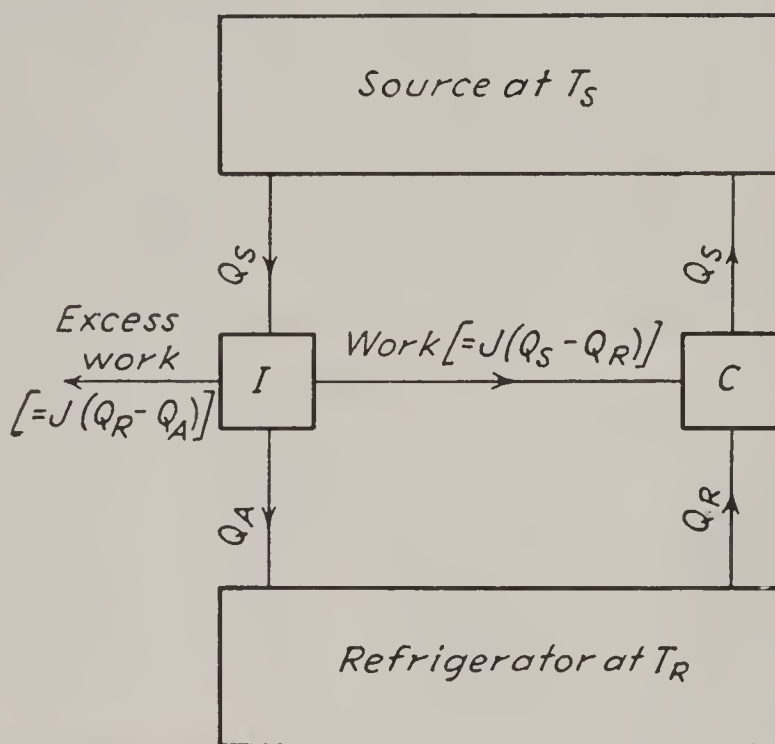


FIG. 5:2. The Carnot principle.

Law, and the assumption with which this analysis began must be rejected as impossible. The Carnot principle is therefore confirmed.

Two important corollaries of the Carnot principle are stated below:

1. *All reversible engines, when operating between the same temperatures of source and refrigerator, will have the same efficiency.*
2. *The efficiency of a reversible engine will depend only on the temperatures of the source and the refrigerator and will be independent of the working substance.*

The method of proof of each of these corollaries is similar in character to the proof of the Carnot principle; it is assumed that the opposite is true, and this assumption is then shown to be absurd. The detailed steps in each proof are left to the reader.

The first corollary indicates that the reversible Stirling engine would have the same efficiency as the Carnot engine when operating under equivalent conditions and could therefore replace the Carnot as a device for evaluating Second Law effects. That the Carnot engine is the accepted tool for the purpose is due in part to the greater simplicity of the cycle on which it operates in that heat exchange takes place only with



source and refrigerator and there is no necessity for regeneration (see Art. 4:6).

The second corollary leads directly to the concept of a thermodynamic scale of temperature to be discussed in the following article.

**5:6. The Thermodynamic Scale of Temperature.** To Carnot is credited the discovery that the maximum thermal efficiency possible for a heat engine is that of a reversible engine and that this maximum efficiency is some function of the temperatures of source and refrigerator. In Carnot's time temperatures were based on arbitrarily chosen properties of the thermometer. Within the range of the thermometer the relative hotness of an object could be determined and compared with those of other objects but on only a qualitative basis. The temperatures of a number of objects furnished a means of arranging these in order of their hotness; beyond that, temperature had little significance except that temperatures were reproducible and that equality of temperature could therefore be established.

When he advanced his theory, Carnot had no knowledge of what function of the temperatures of source and refrigerator represented the efficiency of the reversible engine. It remained for Lord Kelvin, a quarter of a century later, to realize the significance of Carnot's discoveries and to suggest that, based on the efficiency of the reversible engine, a temperature scale could be devised that would be independent of any property of the thermometric substance. The temperature scale which Kelvin proposed might well be called the *thermodynamic scale of temperature*.

Suppose three reservoirs at temperatures  $t_1$ ,  $t_2$ , and  $t_3$ , of which  $t_1$  is the hottest and  $t_3$  the coldest as illustrated in Fig. 5:3. A reversible engine  $A$  will receive heat at a rate that will be designated as  $Q_1$  from the reservoir at  $t_1$  (acting as its source) and discharge heat at the rate  $Q_2$  to the reservoir at  $t_2$  as its refrigerator. A second reversible engine  $B$  will receive heat at the rate  $Q_2$  from the reservoir at  $t_2$  (which thus acts as its source) and will discharge heat at the rate  $Q_3'$  to the reservoir at  $t_3$  as its refrigerator. By the First Law, engine  $A$  will deliver work at a rate equal to the difference between  $Q_1$  and  $Q_2$ , or  $Q_1 - Q_2$ , and engine  $B$  will have a rate of work delivery equal to  $Q_2 - Q_3'$ .

Reversible engine  $C$  is placed between the reservoir at  $t_1$  and the reservoir at  $t_3$ , the first acting as its source and the second as its refrigerator. It will be operated simultaneously with engines  $A$  and  $B$  and at a rate such that  $Q_1$  units of heat are drawn from the source in the same time that this reservoir supplies the same amount of heat to engine  $A$ . The rate at which it rejects heat to its refrigerator, the reservoir at  $t_3$ , will be designated as  $Q_3$ , and its work output is therefore at the rate  $Q_1 - Q_3$ .

For  $Q_1$  units of heat removed from the reservoir at  $t_1$ , the sum of the

work output of engines  $A$  and  $B$  is  $Q_1 - Q_3'$ , and the work output of engine  $C$  is  $Q_1 - Q_3$ . If  $W_A + W_B > W_C$ , engine  $C$  may be reversed and driven as a heat pump by means of power furnished by engines  $A$  and  $B$ , leaving a surplus of power for other purposes. A violation of the Second Law will be the result since the reservoirs at  $t_1$  and  $t_2$  will both be acting merely as conductors, there being no net heat flow to or from them, and the surplus of power mentioned above is solely at the expense of heat

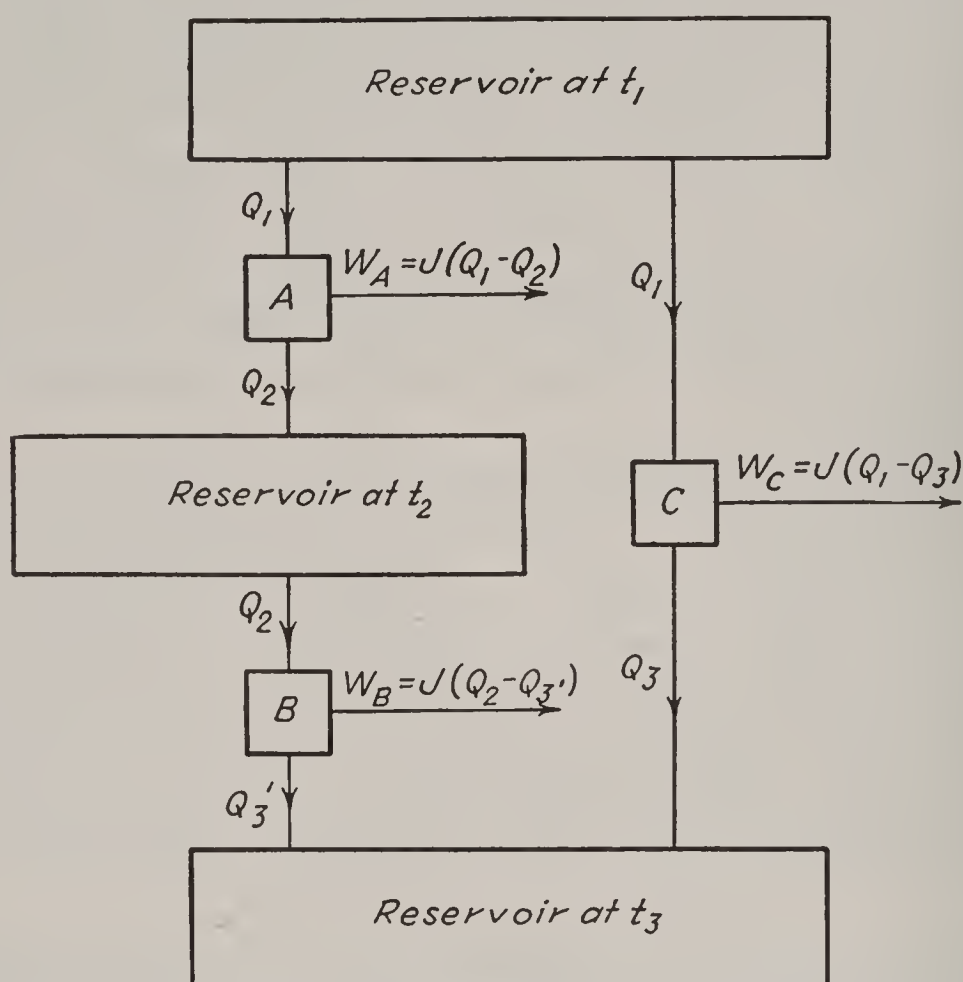


FIG. 5:3. The concept of a thermodynamic scale of temperature.

taken from the reservoir at  $t_3$ . If, on the other hand,  $W_C > W_A + W_B$ , the reversal of engines  $A$  and  $B$  to act as heat pumps will produce the same result. Therefore  $W_A + W_B = W_C$ ,  $Q_1 - Q_3' = Q_1 - Q_3$ , and  $Q_3' = Q_3$ .

Equation (2:15) may be expressed as

$$\eta = 1 - \frac{Q_R}{Q_S} \quad (5:1)$$

As it applies to the conditions illustrated in Fig. 5:3, this equation would become  $\eta = 1 - Q_3/Q_1$  and this would be the efficiency of both engine  $C$  and the combination of engines  $A$  and  $B$ . As the temperature of the reservoir at  $t_3$  was decreased, the efficiency would increase and  $Q_3$  would correspondingly decrease. This could be used as the basis of a temperature scale on which  $t_3$  could be rated with respect to  $t_1$  in the proportion that  $Q_3$  bears to  $Q_1$ . Let us temporarily designate temperatures on this



proposed thermodynamic scale of temperature as  $\theta_1, \theta_2, \theta_3$ , etc. Then

$$\frac{Q_3}{Q_1} = \frac{Q_R}{Q_S} = \frac{\theta_3}{\theta_1} = \frac{\theta_R}{\theta_S} \quad \text{and} \quad \eta_{\text{rev engine}} = 1 - \frac{\theta_R}{\theta_S} = \frac{\theta_S - \theta_R}{\theta_S} \quad (5:2)$$

The Kelvin and Rankine scales of temperature were devised to meet the requirements of this thermodynamic scale of temperature, and they vary so slightly from it that  $T$  on either scale may be substituted for  $\theta$  in Eq. (5:2). The efficiency of a reversible engine when operating between two reservoirs may then be stated as

$$\eta_{\text{rev engine}} = 1 - \frac{T_R}{T_S} = \frac{T_S - T_R}{T_S} \quad (5:3)$$

Naturally, the same scale of absolute temperature must be used to express both  $T_S$  and  $T_R$  when substitution is made in Eq. (5:3).

*Example 5:6.* Using Eq. (5:3), calculate the efficiency of the Carnot and Stirling engines of Examples 4:9 and 4:10.

*Solution.* For both engines,

$$\eta = \frac{T_S - T_R}{T_S} = \frac{960 - 560}{960} = 0.417$$

This answer agrees with the result of the calculation of the efficiency as carried out in the two examples.

As the efficiency of the reversible engine increased toward unity as a limit,  $Q_R$  would correspondingly decrease until the heat discharged to the refrigerator became zero. This would also constitute a zero point on the thermodynamic scale of temperature. As the temperature of the refrigerator declined below this point and became negative, it would be noted that the heat rejected to the refrigerator would have become a heat supply from that reservoir. This energy and that which the engine received from its source could be replaced by heat flow from a single reservoir at a temperature that was sufficiently high, and a violation of the Second Law would be apparent. *It is impossible to attain negative temperatures on the thermodynamic scale of temperature.* The corresponding temperature on the Kelvin and Rankine scales is therefore designated as the *absolute zero* of temperature.

The lowest temperature that develops as the result of natural processes on the earth's surface is about 200°K. In order to demonstrate temperatures which approach absolute zero it is therefore necessary to employ some kind of "heat pump" to draw heat from the body to be cooled, as the refrigerator, and discharge it to a reservoir at some higher level of temperature. When, as the result of the removal of this heat, the temperature of the cold body approaches absolute zero, the ratio of the work required to drive the heat pump to the heat withdrawn from the cold body

approaches infinity. Unless the cold body may be perfectly insulated, which is never possible in practice, it is in the meantime receiving heat at a finite rate from surrounding systems. *In the absence of a perfect insulator, absolute zero of temperature cannot be attained.*

### Problems

1. For any of the nonflow processes outlined in Prob. 13, Chap. 4, which you decide are irreversible, show that a perpetual-motion machine of the second kind would result if the process were reversible.

2. Show, for each of the irreversible processes described in Prob. 14, Chap. 4, that a perpetual-motion machine of the second kind would be required to make it reversible.

3. In Example 2:10 it was shown that it was possible to change all of the heat received by a system from a source at constant temperature into work as the result of an isothermal process. Why is this not a violation of the Second Law?

4. A system consisting of an *electric motor and connected storage battery* can deliver work to surrounding systems and, at the same time, give off heat to the surroundings. Why is this not a violation of the Second Law?

5. Prove the first corollary of the Carnot principle.

6. Prove the second corollary of the Carnot principle.

7. Prove that a system which is not receiving work cannot convey heat from a cold to a hot body continuously. Describe a system which might do so over a limited period of time.

8. Two Carnot engines  $A$  and  $B$  both receive heat from the same source at an unknown thermodynamic temperature which will be designated as  $\theta_1$ . Both receive heat at the same rate  $Q_1$ , but the magnitude of  $Q_1$  is not known. Carnot engine  $A$  discharges heat to a sink of unknown temperature  $\theta_2$  and delivers a known amount of power. Engine  $B$  employs a sink of unknown temperature  $\theta_3$  and delivers half the power of engine  $A$ . Based only on the information as stated above, which of the following statements are necessarily true? (a) The efficiency of engine  $A$  is twice that of engine  $B$ . (b)  $\theta_3 = 2\theta_2$ . (c)  $\theta_2 = 2\theta_3$ . (d)  $\theta_1 - \theta_2 = 2(\theta_1 - \theta_3)$ . (e) The ratio  $\theta_3/\theta_2$  may be computed. (f) The efficiency of engine  $A$  may be computed.

9. Same as Prob. 8 except that  $Q_1$  is known in magnitude.

10. What is the maximum possible efficiency of an engine that receives heat from a source at  $1000^\circ\text{F}$  and discharges heat to a sink at  $70^\circ\text{F}$ ?

11. A Carnot engine delivers 50 hp while receiving heat from a source at  $800^\circ\text{F}$  and discharging heat to the atmosphere at  $60^\circ\text{F}$ . At what rate, in Btu per minute, does it receive heat? What is its efficiency?

12. A reversible engine which does not operate on the Carnot cycle receives 100 Btu of heat per second from a constant-temperature source at  $600^\circ\text{F}$  and delivers 70 hp. If the temperature of its refrigerator is constant, what is that temperature?

13. A Carnot engine that uses gas  $W$  as its working substance operates between source and sink temperatures of  $1200$  and  $100^\circ\text{F}$ . What is its efficiency? How would your answer have been affected if the working substance had been gas  $Y$ ? If it had been a nonideal gas? If it had been steam?

14. A Carnot engine has an efficiency of 40 per cent and rejects heat at the rate of 12,000 Btu/hr to a refrigerator at  $70^\circ\text{F}$ . What is the temperature of its source? What horsepower does the engine deliver?

15. A reversible engine discharges 200 Btu/min to a refrigerator at a constant temperature of  $40^\circ\text{F}$  while delivering 5 hp. What is the (constant) temperature of its source? What is its efficiency?



16. A Carnot engine uses an ideal gas as its working substance. At the end of the isothermal expansion, the pressure of the gas is 100 psia, and the volume of the contained system is 4 ft<sup>3</sup>. At the end of the adiabatic expansion, the pressure is 20 psia, and the volume is 12.6 ft<sup>3</sup>. What is the efficiency of the engine?

17. At the beginning of the isothermal expansion, the pressure and volume of the ideal-gas system that is the working substance of a Carnot engine are 50 psia and 1 ft<sup>3</sup>, respectively. At the end of the adiabatic expansion, the pressure is 15 psia, and the volume 2.5 ft<sup>3</sup>. What is the efficiency of the engine?

18. A reversed Carnot engine removes 12,000 Btu/hr from a refrigerator at 10°F and discharges heat to the atmosphere at 90°F. What horsepower is required to drive it?

19. A building that requires 100,000 Btu/hr to maintain its temperature at 70°F when the outside temperature is 20°F is to be heated by means of a reversed Carnot engine. What horsepower will be required to drive the engine? At what rate is heat removed from the outside air?

### Symbols

- $Q$  rate of heat flow, per cycle or per unit time  
 $t$  scalar temperature  
 $T$  absolute temperature  
 $W$  rate of work delivery, per cycle or per unit time

### Greek Letters

- $\eta$  efficiency of a heat engine  
 $\theta$  temperature on the thermodynamic scale

### Subscripts

- $R$  refrigerator  
 $S$  source

## CHAPTER 6

### ENTROPY, A PROPERTY OF THE SYSTEM

**6:1. Entropy.** It has been observed that it is possible to represent the work which accompanies a reversible process (a maximum-work process) on a diagram of which the coordinates are the pressure and the volume, both being properties of the system. A diagram that would perform the same function for the heat flow which takes place during a reversible process would be of equal or even greater usefulness. With reference to the maximum-work diagram, pressure is an intensive, volume an extensive property. Pressure may be regarded as that property which furnishes the incentive, or potential, for the system to do work. Differentials of pressure, infinitesimal for the reversible process, determine the direction of work flow. The property with respect to heat flow which is analogous to absolute pressure on the work diagram is temperature since differences in temperature determine the direction of heat flow. Absolute temperature therefore will be used as the ordinate on the diagram for which we are searching.

The second dimension, which must be a property of the system since a plotted point on the diagram must definitely establish a unique state of the simple system, is more difficult of selection. This dimension may, however, be determined in terms of the quantities by which it must be measured. We may rewrite Eq. (2:6) in differential form as  $\partial W = P dV$ . Equation (2:6) is valid only for a reversible process and, transposing,

$$dV = \frac{\partial W}{P} \quad (\text{reversible}) \quad (6:1)$$

Following the analogy which is proposed above, if we designate the sought-after property by the symbol  $S$ , then

$$dS = \frac{\partial Q}{T} \quad (\text{reversible}) \quad (6:2)$$

Equation (6:2) defines a quantity which we shall call *entropy* (en'tropy). If entropy can be shown to be a property of the system, the temperature-entropy diagram will have the same usefulness with respect to the measurement of reversible (maximum) heat flow that the pressure-volume diagram possesses in connection with the calculation of the maximum work which may accompany a given path.

It remains to be proved that entropy is a property of the system. One



of the methods of proof of the status of a quantity as a property of the system that was outlined in Chap. 1 consisted in showing that its line integral around any cycle was zero. If it can be shown that the line integral of  $\partial Q/T$  (reversible) is always zero, then the line integral of  $dS$  must be zero around any cycle and entropy will assume the status of a property of the system. The proof that the line integral of  $\partial Q/T$  is zero around any *reversible* cycle is equivalent to the requirement as set forth above, and this proof will be the next step in our discussion.

Temperature and volume have approved status as independent properties of the system. We may, as in Fig. 6:1, represent *any reversible cycle* on these coordinates by the closed curve  $R$  of that figure. The area enclosed within  $R$  will be divided into curved strips by the lines  $a$ , which represent the paths followed during reversible adiabatic processes. Each pair of adjacent adiabatics may then be joined at the top and the bottom by horizontal lines  $i$ , which will intersect the curve  $R$  as shown. These horizontal lines represent reversible isothermals and, together with the reversible adiabatic lines which they connect, form individual Carnot cycles into which the entire area enclosed within  $R$  is divided. As the distance between the lines  $a$  is reduced, the contour of the outline of these Carnot cycles will approach the closed curve  $R$ .

For each of the individual Carnot cycles it has been shown in Art. 5:6 that  $Q_S/T_S = Q_R/T_R$  [see Eq. (5:2)]. Since the heat transfers during the reversible isothermal processes take place at constant temperature,  $Q/T$  may replace  $\int \partial Q/T$  (reversible). But  $Q_R$  represents a rejection of heat by the working substance and, taking the sign of the heat flow into consideration,

$$\frac{Q_S}{T_S} + \frac{Q_R}{T_R} = 0 \quad (6:3)$$

In other words, the increase of the quantity along the upper isothermal is equaled by its decrease along the lower. The curved sides of each of these small cycles are reversible adiabatics during which there is no heat flow and for which  $\int \partial Q/T$  is zero. The total change of the quantity around each of these segmentary cycles is therefore zero. But these cycles, taken together, duplicate the reversible cycle  $R$  as a limit, and we obtain

$$\oint \frac{\partial Q}{T} \text{ (reversible)} = 0 \quad (6:4)$$

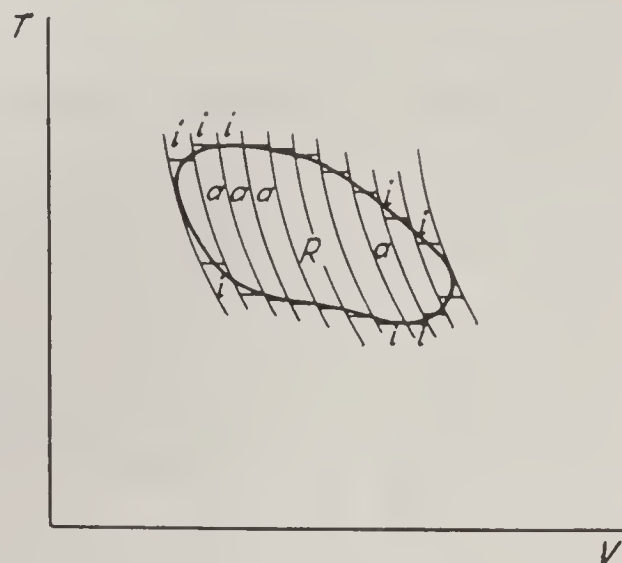


FIG. 6:1. Entropy as a property.

*Example 6:1A.* Calculate the total change of entropy around the Carnot cycle of Example 4:9.

*Solution:*

$$\text{For the reversible process 1-2, } S_2 - S_1 = \int_1^2 \frac{\partial Q}{T} = \frac{Q_S}{T_S} = \frac{45.5}{960} = 0.0473$$

$$\text{For the reversible process 2-3, } S_3 - S_2 = \int_2^3 \frac{\partial Q}{T} = \frac{0}{T} = 0$$

$$\text{For the reversible process 3-4, } S_4 - S_3 = \int_3^4 \frac{\partial Q}{T} = \frac{-Q_R}{T_R} = \frac{-26.5}{560} = -0.0473$$

$$\text{For the reversible process 4-1, } S_1 - S_4 = \int_4^1 \frac{\partial Q}{T} = \frac{0}{T} = 0$$

$$\text{Around the reversible cycle, } \oint \frac{\partial Q}{T} = \oint dS = 0.0473 + 0 + (-0.0473) + 0 = 0$$

The basic criterion on which the status of a quantity as a property is established is that its change between two given states of the system is independent of the path or process which is traversed by the system during that change of state. It may be shown that this requirement is satisfied for entropy if Eq. (6:4) is valid. Let two reversible cycles 1-*m*-2-*n* and 1-*m*-2-*p*, respectively, be plotted on a diagram having as its coordinates any two independent properties of the system  $P_1$  and  $P_2$ , as illustrated in Fig. 6:2. These cycles have a common reversible process 1-*m*-2 for which  $\int_1^2 \frac{\partial Q}{T}$  (reversible) is evidently the same for both cycles. But,

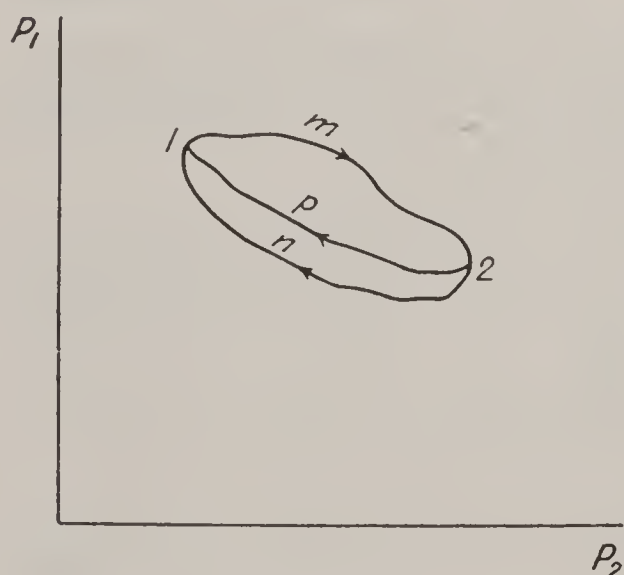


FIG. 6:2. Entropy as a property.

based on Eq. (6:4), the line integral of  $\partial Q/T$  around either of these cycles must be zero, and we may therefore conclude that the total change of the quantity  $\partial Q/T$  between the states represented by points 2 and 1 will be the same for any *reversible* process that may connect them. For the measurement of the change of entropy between the two states a reversible process must be selected if that change of entropy is to be evaluated as  $\int \partial Q/T$ . For it is only in connection with the reversible proc-

ess that the definition of entropy which is implied in Eq. (6:2) is valid. However, having established the amount by which the entropy has changed by applying Eq. (6:2) to any reversible process that connects the two states, this change of entropy will apply whenever the system changes from one state to the other even if the process that connects them is irreversible.

Let us illustrate this important point more forcibly by returning to our analogy in which the proposed diagram for the measurement of heat flow



during a reversible process was compared with the pressure-volume diagram and its use in measuring work transfer during the reversible (maximum-work) process. Referring to Fig. 6:3, let the full lines  $m$  and  $n$  between points 1 and 2 represent the paths followed during any two reversible processes that connect these states of the system. The dashed line  $i$  will represent the path traversed during a third, but irreversible, process which has its inception at state 1 and ultimately brings the system to state 2. It has been shown that the maximum work that may accompany a given path will be developed when that path is carried out reversibly and that the amount of this work is represented by the area under the path on a pressure-volume diagram. Thus the strip areas  $\partial W_m$  and  $\partial W_n$  represent the work done by the system as segments of the reversible paths  $m$  and  $n$ , respectively, are traversed. Equation (6:1) may be applied to

find the elementary change of volume that took place, and the integration of these infinitesimal volume changes over the entire process would result in the total change of volume during the process, or  $V_2 - V_1$ . Further, no matter which of these reversible processes was used, the total change of volume would be the same. Now let us consider the same method as applied to the irreversible process  $i$ . A strip area  $A_i$  (shown within dashed lines) may again be associated with a segment of this path, and, following the same procedure as for the reversible processes  $m$  and  $n$ , the

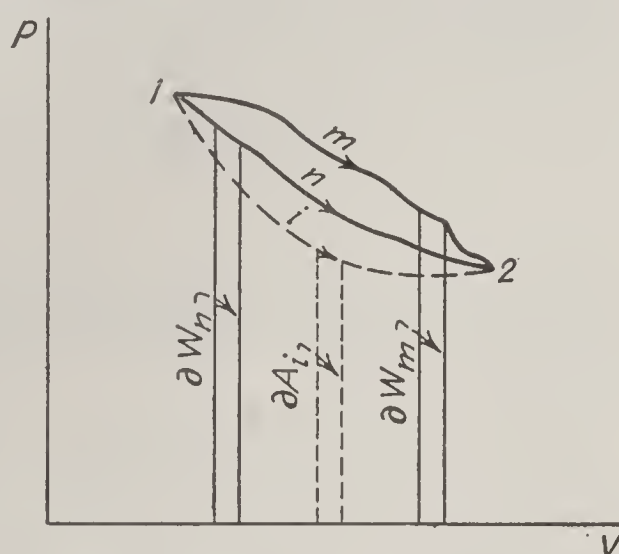


FIG. 6:3. Evaluation of change in volume.

change of volume may be evaluated as  $V_2 - V_1 = \int_1^2 \frac{\partial A_i}{P}$ . But in this

case the area of the strip does not represent the work that accompanied the elementary change of volume. Instead we know that this work is less than the segmentary area since the process is irreversible and therefore  $\partial W_i < \partial A_i$ . Returning to Eq. (6:1), we have seen that it is correct to

write  $dV = \partial A_i / P$  and  $V_2 - V_1 = \int_1^2 \frac{\partial A_i}{P}$ . Since  $\partial W_i < \partial A_i$ , it is incorrect to substitute  $\partial W_i$  for  $\partial A_i$  in these equations, but inequalities may be written, as follows:

$$dV > \frac{\partial W}{P} \quad (\text{irreversible}) \quad \text{and} \quad V_2 - V_1 > \int_1^2 \frac{\partial W}{P} \quad (\text{irreversible}) \quad (6:5)$$

To include both reversible and irreversible processes in their scope, Eqs.

(6:5) could be written

$$dV \geq \frac{\partial W}{P} \quad \text{and} \quad V_2 - V_1 \geq \int_1^2 \frac{\partial W}{P} \quad (6:6)$$

In this form they would apply to *any* process. The equality would, of course, apply to any *reversible* process [see Eq. (6:1)].

To conclude our application of the analogy, note that the same total change of volume was obtained by applying Eq. (6:1) over any reversible process connecting states 1 and 2 of the system and that this change of volume, though not in that case obtainable as the integral of  $\partial W/P$ , also applied to any irreversible process connecting those states. Just as the work is a maximum for a reversible process, so is the heat flow also a maximum (see Chap. 2), and we may write expressions for the change of entropy analogous to Eqs. (6:6),

$$dS \geq \frac{\partial Q}{T} \quad \text{and} \quad S_2 - S_1 \geq \int_1^2 \frac{\partial Q}{T} \quad (6:7)$$

The equality again applies to the reversible process. The inequality is in the algebraic sense that has previously been applied in the definition of maximum work.

Summarizing, *since entropy is a property, its change will be independent of the process by which a change of state is effected and will depend only on the end states. The integral of  $\partial Q/T$  may be used to evaluate the change of entropy only in a reversible process connecting the given end states.*

*Example 6:1B.* The rate of heat flow to a system per unit increase of temperature during a certain reversible process is constant and equal to 0.7 Btu/°F. (a) Calculate the change of entropy during the process if the initial temperature is 100°F, the final temperature 300°F. (b) A second process which follows the same path between the same end states is accompanied by heat flow at a rate half as great as in part a. What is the change of entropy for this second process? (c) A third process connects the same end states over an entirely different path. What is the change of entropy?

*Solution:*

$$(a) \frac{\partial Q}{dt} = 0.7 \text{ or } \partial Q = 0.7 dt = 0.7 dT$$

$$S_2 - S_1 = \int_1^2 \frac{\partial Q}{T} \text{ (reversible)} = 0.7 \int_{T_1}^{T_2} \frac{dT}{T} = 0.7 \log_e \frac{760}{560} = (0.7)(0.306) = 0.214$$

(b) The second process is evidently not reversible since the heat flow is less than the maximum that could accompany the given path. Thus the change of entropy is not obtainable as the integral of  $\partial Q/T$ . But the process connects the same end states as in part a, and since entropy is a property, the change of entropy will be the same, or  $S_2 - S_1 = 0.214$ .

(c) No matter what path or process connected these two end states, the change of entropy, a property of the system, would be the same. Therefore,  $S_2 - S_1 = 0.214$ .

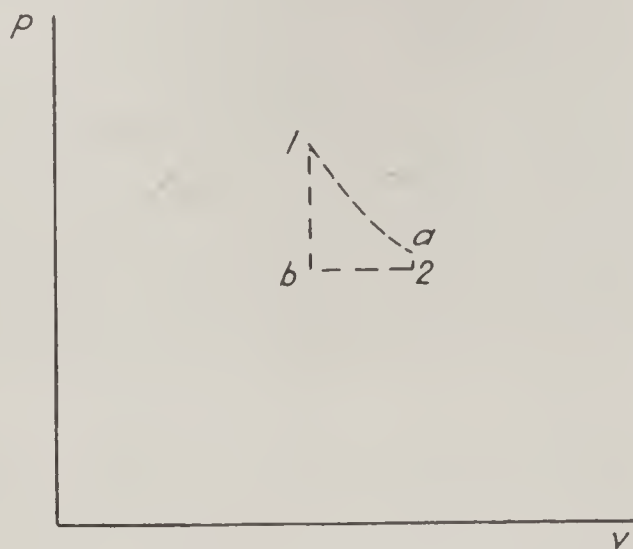


In evaluating changes of entropy it will be remembered that  $\partial Q = dU + P dV/J$  for the simple closed system during a reversible process [see Eqs. (2:5) and (2:6)], and Eq. (6:2) may therefore be changed to the form

$$dS = \frac{dU}{T} + \frac{P dV}{JT} \quad (6:8)$$

This equation indicates that entropy is an extensive property since both the change of internal energy and the change of volume of the system with respect to a given change in its pressure and temperature will depend upon the mass of the system. The lower-case letter  $s$  will be used to designate specific entropy, or entropy per pound. The unit of entropy, since it is the quotient obtained by dividing the heat flow (Btu) by the absolute temperature, may be stated as Btu per degree Rankine if we employ the system of units used in this text. This unit of entropy is sometimes called the "rank." It is customary in technical literature to omit any designation of the unit of entropy that is employed and allow it to be inferred from the context. Thus another unit of entropy might be the calorie per degree Kelvin.

*Example 6:1C.* One pound of a substance having an equation of state as in Example 1:10 changes from an initial state at which  $p_1 = 30$  psia,  $v_1 = 10$  ft<sup>3</sup>, to a final



pressure and final volume of 20 psia and 14 ft<sup>3</sup>, respectively. Calculate the difference of entropy between the two states by applying Eq. (6:8).

*Solution.* The required difference of entropy may be calculated as the integral of  $dU/T + P dV/JT$  over *any* path that connects these states. Two paths will be selected for the purpose, the change of entropy over each will be calculated, and the results will be compared. The first path will proceed from state 1 at constant temperature until the volume corresponding to state 2 is reached and thence at constant volume to state 2. This path is shown as path 1-a-2 in the figure that accompanies this example. Then

$$T_a = T_1 = \frac{(30)(10)}{0.37} = 811^\circ\text{R}; T_2 = \frac{(20)(14)}{0.37} = 757^\circ\text{R}; v_a = v_2 = 14 \text{ ft}^3$$

$$p_a = \frac{(0.37)(811)}{14} = 21.4 \text{ psia}$$

For segment 1-*a* of this path, from Eqs. (1:6) and (1:7),

$$du = 0.46 d(pv) = (0.46)(0.37) dT = 0.17 dT = 0; p = \frac{CT}{v} = \frac{(0.37)(811)}{v} = \frac{300}{v}$$

$$\frac{P dv}{JT} = \frac{144p dv}{778} = \frac{(144)(300) dv}{(778)(811)v} = 0.0684 \frac{dv}{v}$$

$$s_a - s_1 = \int_1^a \frac{du}{T} + \int_1^a \frac{P dv}{JT} = \int_1^a \frac{0}{T} + 0.0684 \int_{v_1}^{v_a} \frac{dv}{v} = 0.0684 \log_e \frac{14}{10} = 0.0231$$

For segment *a*-2,  $du = 0.17 dT$  and  $P dv = 0$ ,

$$s_2 - s_a = \int_a^2 \frac{du}{T} + \int_a^2 \frac{P dv}{JT} = 0.17 \int_{T_a}^{T_2} \frac{dT}{T} + \int_a^2 \frac{0}{T} = 0.17 \log_e \frac{757}{811} = -0.0117$$

$$s_2 - s_1 = (s_a - s_1) + (s_2 - s_a) = 0.0231 - 0.0117 = 0.0114$$

Let us now select a second path which will proceed from state 1 at constant volume to state *b* at which the pressure is the same as at state 2 and thence at constant pressure until state 2 is reached. This path is also shown on the figure. Then,

$$p_b = p_2 = 20 \text{ psia}; v_b = v_1 = 10 \text{ ft}^3; T_b = \frac{(20)(10)}{0.37} = 541^\circ\text{R}$$

For segment 1*b*,  $du = 0.17 dT$  and  $P dv = 0$  as shown above.

$$s_b - s_1 = 0.17 \log_e \frac{541}{811} = -0.0690$$

For segment *b*-2,  $du = 0.17 dT$ . The pressure is constant and therefore, from Eq. (1:6),  $p dv = C dT = 0.37 dT$ ,

$$\frac{P dv}{JT} = \frac{(144)(0.37) dT}{778T} = 0.0684 \frac{dT}{T}$$

$$\begin{aligned} s_2 - s_b &= \int_b^2 \frac{du}{T} + \int_b^2 \frac{P dv}{JT} = 0.17 \int_{T_b}^{T_2} \frac{dT}{T} + 0.0684 \int_{T_b}^{T_2} \frac{dT}{T} = 0.2385 \int_{T_b}^{T_2} \frac{dT}{T} \\ &= 0.2385 \log_e \frac{757}{541} = 0.0804 \end{aligned}$$

$$s_2 - s_1 = (s_b - s_1) + (s_2 - s_b) = -0.0690 + 0.0804 = 0.0114$$

This result agrees with that obtained by the calculation which was based on the path 1-*a*-2.

In utilizing this new property we shall differ in one respect from the methods used in connection with the analogous coordinate (volume) on the pressure-volume diagram. Volume may be, and usually is, measured in absolute terms although in connection with paths, processes, and cycles it is *changes* of volume that are of principal interest. The *Third Law* of thermodynamics states that *the entropy of a system is zero when the temperature of the system is the absolute zero of temperature*, and it is conceivable that the *absolute* value of the entropy corresponding to a given state of the system could be calculated by integrating  $\partial Q/T$  over some reversible path connecting a state at absolute zero to the given state. Inadequacy of available data at low levels of temperature makes this procedure impractical, and it is customary either to content ourselves with a calculation of the change of entropy between states in which we are interested or, for the purpose of tabulating the values of entropy corresponding to various



states of the system, to select some convenient reference point at which the entropy is arbitrarily given a value of zero. This completely serves our purpose since it is the changes of entropy with which we shall be concerned in practical thermodynamic computations rather than its absolute values. Note also that in the first steps of the procedure that is suggested above for the calculation of absolute entropy the change of entropy would be disproportionately large because of the low value of the denominator of  $\partial Q/T$ .

Entropy is an abstract quantity. It cannot be observed as volume is observed and tangibly evaluated. Let us now see whether or not the effort that has been expended on the development of this new property promises to be rewarding.

### 6:2. The Temperature-Entropy Diagram and the Reversible Process.

Figure 6:4 shows a diagram for which the ordinate is the absolute temperature and the abscissa is the entropy. The path 1-2 represents a *reversible* process which is executed by a given simple closed system. The segmental area under this path which is shown in the figure has a height  $T$  and a width  $dS$ . From Eq. (6:2) its area is  $\partial Q$ , an element of heat flow. When  $dS$  is positive, as in moving to the right along the reversible path 1-2, this heat flow is positive and represents a passage of heat into the system; the opposite is true when the change of entropy is negative.

Because a simple system is involved and entropy now has the status of a property, the path 1-2 represents a succession of states of the system and that path could be transferred to a pressure-volume chart since any two independent properties of the simple system (in this case the temperature and the entropy) will fix the values of all other properties. Also it has been shown previously that, if the process is reversible, the path must connect equilibrium states.<sup>1</sup>

The total area under the path (area 1-2-b-a), being the summation of elementary areas similar to that illustrated in the figure, represents the total heat flow that accompanies reversible process 1-2. Conversely, the

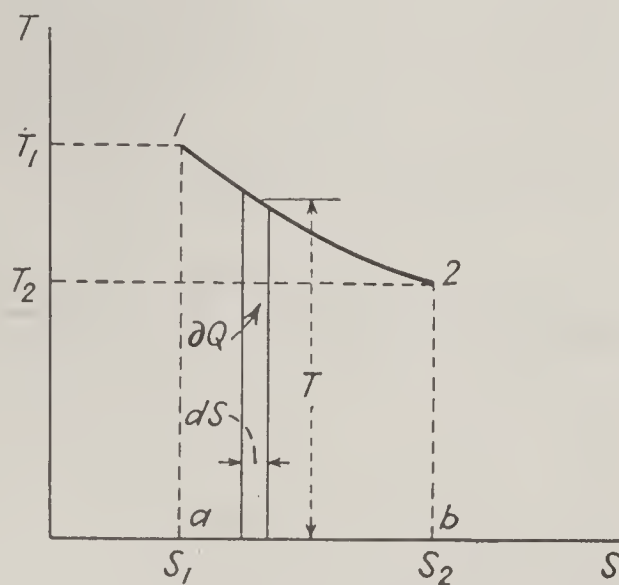


FIG. 6:4. The  $TS$  diagram and the reversible process.

<sup>1</sup> It is emphasized that this discussion applies only to the case when the process is reversible. If irreversible, the inequality [see Eq. (6:7)] will apply and  $\partial Q < T dS$ . For the irreversible process the path will be impossible to trace if it does not connect equilibrium states, but points may be established, as discussed in Art. 2:11, by stopping the process at intervals and allowing the system to assume an equilibrium state.

change of entropy that takes place as the path is reversibly traversed can be found, by applying Eq. (6:2), to be [see Eqs. (6:7) and (6:8)]

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\partial Q}{T} (\text{reversible}) = \int_1^2 \frac{dU}{T} + \int_1^2 \frac{P dV}{JT} \quad (6:9)$$

Let us apply Eq. (6:9) to the problem of locating certain of the reversible processes discussed in Chap. 2 as corresponding paths on the temperature-entropy diagram.

*Example 6:2A.* During a reversible process that is represented by a straight line on a temperature-entropy diagram, the temperature of a system increases from 40 to 200°F as its entropy decreases by 0.1 rank. What heat flow accompanies the process?

*Solution.* The process is stated to be reversible, and the area under the path on the  $TS$  diagram therefore will measure the required heat flow. This area is trapezoidal, and thus

$${}_1Q_2 = \frac{T_1 + T_2}{2} \Delta S = \left( \frac{500 + 660}{2} \right) (-0.1) = -58 \text{ Btu}$$

It will be observed that the change of entropy supplies the same criterion for the determination of the direction of heat flow during a reversible process as the change of volume furnishes for the sign of work performed. For just as a continuous increase of volume throughout a reversible process indicates that the work of the process is positive, so a continuous increase of entropy indicates positive heat flow *provided that the process is reversible*.

*The Reversible Isothermal.* The reversible-isothermal, or constant-temperature, path would of course appear as a horizontal line on the  $TS$

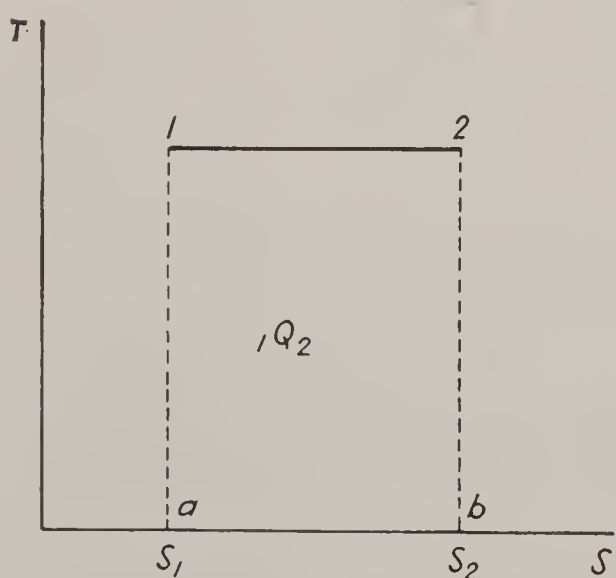


FIG. 6:5. The  $TS$  diagram and the isothermal process.

diagram. It is represented by path 1-2 in Fig. 6:5. The heat flow that accompanies this process is easily measurable as the rectangular area 1-2-b-a or as  $T(S_2 - S_1)$ . Here an advantage of the  $TS$  diagram as compared with the  $PV$  diagram makes its appearance. If it is necessary to calculate the heat flow that takes place during a reversible isothermal process and the  $PV$  diagram is our only tool for the purpose, the procedure as outlined in Chap. 2 consists of three steps, as follows:

1. Measure the area under the path on a  $PV$  diagram, and so obtain the work that accompanies the process.
2. Calculate the change of internal energy that takes place between states 1 and 2 by applying an appropriate equation of state.
3. Substitute the values obtained by carrying out the first two steps in



Eq. (2:3), and thereby obtain the heat flow that is associated with the process. The temperature-entropy diagram, as a new tool at our command, makes it possible to obtain the heat flow directly as the result of a single simple calculation provided that the entropies at the beginning and the end of the process are known.

*The Reversible Adiabatic.* By definition, no heat flow takes place during an adiabatic process, and if the process is also reversible, there will be no change of entropy.<sup>1</sup> The process is illustrated in Fig. 6:6, path 1-2 being that followed during a reversible adiabatic which is accompanied by a decrease of temperature. Consistent with the definition of an adiabatic, the area under the path is observed to be zero. Again an example of the special usefulness of the temperature-entropy diagram is illustrated. In order to plot successive equilibrium states along a reversible adiabatic path on the pressure-volume diagram, it was first necessary to develop a relationship between the pressure and the volume of the system that would apply along that path (see Example 2:12A) and then to use the resulting equation to plot the path. On the temperature-entropy diagram, on the other hand, the position of all points along the path is fixed by the requirement that the entropy shall not change and the path becomes simply a vertical line.

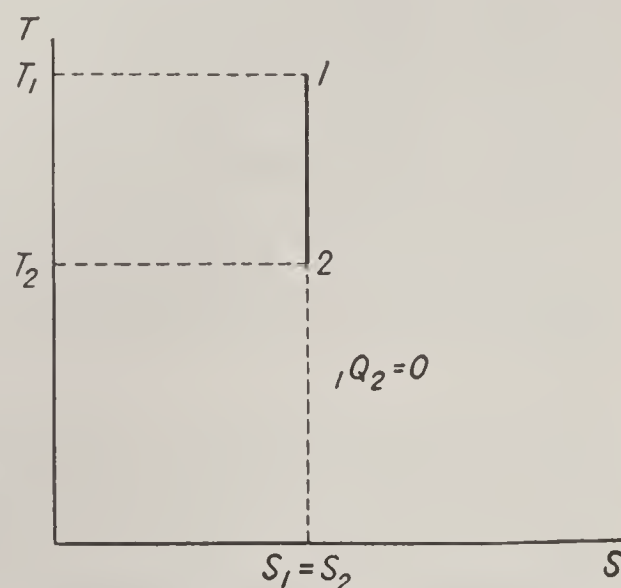


FIG. 6:6. The  $TS$  diagram and the reversible adiabatic process.

*The Reversible Constant-volume and Constant-pressure Paths.* It has been shown that, in any reversible process, the change of entropy may be evaluated as the integral of  $\partial Q/T$ . For a constant-volume reversible process  $\partial Q$  may be replaced by  $M c_v dT$  (see Art. 2:7), and if, for convenience,  $c_v$  may be assumed to have a constant value over the temperature range  $T_1$  to  $T_2$ , then the corresponding change of entropy is

$$S_2 - S_1 \text{ (constant volume)} = M c_v \int_{T_1}^{T_2} \frac{dT}{T} = M c_v \log_e \frac{T_2}{T_1} \quad (6:10)$$

The logarithmic curve that represents Eq. (6:10) is shown in Fig. 6:7 as the curve 1-2. The area 1-2-b-a under this curve is the heat flow which accompanies this constant-volume reversible process. But no work is performed during a constant-volume reversible process, and, referring to

<sup>1</sup> Note that an irreversible adiabatic process could be accompanied by a change of entropy. Equation (6:7) indicates that the entropy would increase during that type of process.

Eq. (2:3), this heat flow (and consequently the area 1-2-b-a) is seen to be equal to the change of internal energy that takes place as a result of the

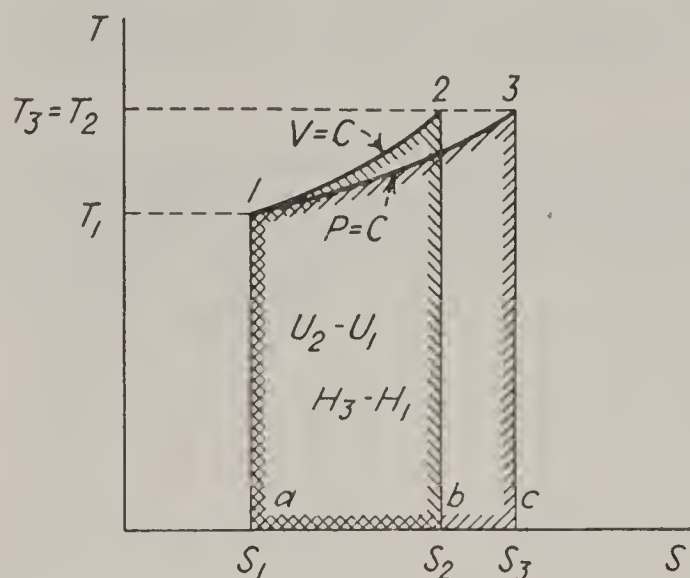


FIG. 6:7. The  $TS$  diagram and the constant-volume and constant-pressure process.

process. This is indicated in Fig. 6:7 by labeling the corresponding area  $U_2 - U_1$ . Moreover, this area would have the same significance in this respect even if path 1-2 had not been specified as reversibly performed, for the change of a property (in this case the internal energy) is dependent only on the end states and will be the same for any path or process that connects the same end states. Thus when the initial and final volumes of the system are equal, even if there was a change of volume in the course of

the process, the change of internal energy will be equal to the area under a path on the  $TS$  diagram which passes through states having equal volumes and connects the given initial and final states.

Proceeding in a similar manner, it may be shown that, with reference to the constant-pressure reversible process of Fig. 6:7,

$$S_3 - S_1 \text{ (constant pressure)} = Mc_p \int_{T_1}^{T_3} \frac{dT}{T} = Mc_p \log_e \frac{T_3}{T_1} \quad (6:11)$$

During any constant-pressure process an increase in the internal energy of the system will accompany an increase in its volume, and vice versa. Since the heat flow during the reversible process must account not only for the change of internal energy but also for the work that results from the changing volume,  $c_p$  is always larger than  $c_v$ . Therefore there will be a larger change of entropy for a given ratio of final to initial absolute temperature of the system during a constant-pressure than over a constant-volume path. This is illustrated in the lesser slope of the constant-pressure path of Fig. 6:7. In this figure  $T_3 = T_2$ , and therefore  $S_3 - S_1 > S_2 - S_1$ . The area 1-3-c-a represents the heat flow if constant-pressure process 1-3 is carried out reversibly. This area, since  $c_p > c_v$  and the constant-pressure and constant-volume processes both take place between the same limiting temperatures, must be larger than the area under path 1-2.<sup>1</sup>

<sup>1</sup> For systems that consist of mixtures of two phases, the specific heat at constant pressure is infinite, *i.e.*, heat may be added reversibly at constant pressure without change of temperature. For this type of system the constant-pressure process is represented by a horizontal line on the  $TS$  diagram.



The area under the constant-pressure path on  $TS$  coordinates, like that under the constant-volume path, has another significance. In Art. 2:8 it was shown that the heat flow during a reversible constant-pressure process was the same as the difference of enthalpy of the system between the end states. The area 1-3-*c*-*a* of Fig. 6:7 therefore represents this change of enthalpy as indicated on the figure. Again, since enthalpy is a property, this same area will represent the change of enthalpy for *any* process that connects the same end states.

*Example 6:2B.* A pound of water at 32°F is converted into steam at a temperature of 250°F. During the process the pressure is atmospheric. The process consists of (a) heating the water to 212°F, (b) evaporating the water to steam at a constant temperature of 212°F, and (c) heating the steam to the final temperature. During part *a* the specific heat is constant at unity, during part *b* 970.3 Btu of heat enters the water, and during part *c* the specific heat may be assumed constant at 0.48. Calculate the total change of entropy.

*Solution:*

$$(a) \Delta S_a = c_p \log_e \frac{672}{492} = (1)(0.312) = 0.312$$

$$(b) \Delta S_b = \frac{Q_b}{T} = \frac{970.3}{672} = 1.445$$

$$(c) \Delta S_c = c_p \log_e \frac{710}{672} = (0.48)(0.0555) = 0.027$$

$$S_2 - S_1 = \Delta S_a + \Delta S_b + \Delta S_c = 0.312 + 1.445 + 0.027 = 1.784$$

### 6:3. The Temperature-Entropy Diagram and the Irreversible Process.

If, for a simple system, the temperature and the entropy of the system are known at a given state, the values of all other properties are fixed and may be calculated if the necessary equations of state are available. This is true whether the given state has been attained as the result of a reversible change or as the end state of an irreversible process. Therefore a constant-volume irreversible process, for instance, may be plotted, and this process will follow exactly the same path as if the process had been reversibly performed. Thus path 1-2 of Fig. 6:7 could as well represent an equivalent irreversible process for which the succession of states was the same as for the reversible process pictured in the figure. However, in the case of an irreversible process, the heat flow would no longer be represented by the area beneath the path. Instead, the heat flow would (in the algebraic sense) be less than this area [see Eq. (6:7) and footnote page 95]. The same principle will hold when any *property* remains constant or when the relation between any two independent properties is known over the path.

It has been shown in Chap. 2 that the path of a reversible adiabatic process for a given system is quite fixed and definite but that a multitude of paths could be traversed if the process were adiabatic but *irreversible*. In Fig. 6:8 are shown a reversible adiabatic process 1-2 and (as 1-3) an

irreversible adiabatic that begins at state 1 and ends at the pressure corresponding to that at point 2. It will be noted that  $S_3 > S_2$  [see Eq. (6:7)] and that it would not be possible for path 1-3 to slope to the left instead of

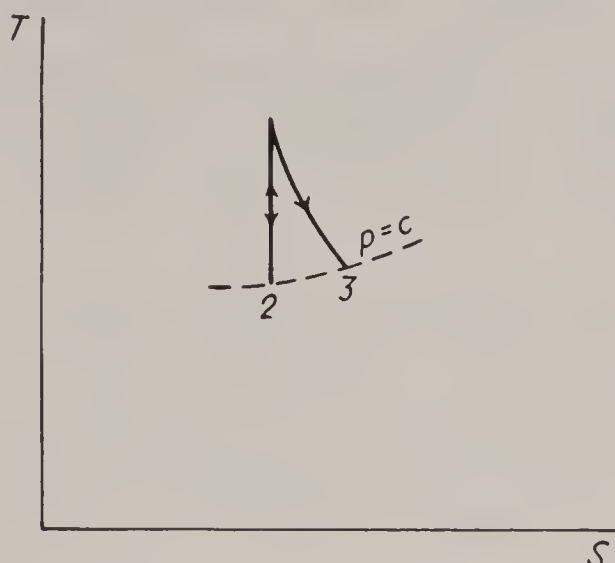


FIG. 6:8. The reversible and the irreversible adiabatic process.

as shown in the figure. The area beneath path 1-3 of course has no heat-flow significance since this path was not traversed during a reversible process. We know only that this area must exceed the heat flow, and this is of course true since the process was specified to be adiabatic.

*Example 6:3.* A system consisting of 1 lb of the gas for which equations of state are given in Example 1:10 has an initial pressure of 60 psia and an initial temperature of 500°F. It expands adiabatically but irreversibly to a final pressure of 10 psia. Because of the

irreversibility the work of the process is 10 per cent less than would have resulted from a reversible adiabatic expansion from the initial state to the final pressure. (a) Calculate the final temperature for the irreversible process, and compare with the temperature at the end of the reversible process. (b) What is the change of entropy that results from the irreversible process?

*Solution.* The notation used will refer to that of Fig. 6-8. Note that  ${}_1Q_2 = {}_1Q_3 = 0$  since both processes are adiabatic and that therefore

$$u_1 - u_2 = \frac{({}_1W_2)_{\max}}{J} \text{ and } u_1 - u_3 = \frac{{}_1W_3}{J} \quad [\text{Eq. (2:3)}]$$

(a) For reversible adiabatic process 1-2,  $p_1 v_1^k = p_2 v_2^k$  [Ex. 2:12A]

$$v_1 = \frac{CT_1}{p_1} = \frac{(0.37)(960)}{60} = 5.92 \text{ ft}^3; v_2 = v_1 \left( \frac{p_1}{p_2} \right)^{1/k} = 5.92 \left( \frac{60}{10} \right)^{1/1.4} = (5.92)(3.59) = 21.25 \text{ ft}^3$$

$$T_2 = \frac{p_2 v_2}{C} = \frac{(10)(21.25)}{0.37} = 574^\circ\text{R, or } 114^\circ\text{F}$$

$$u_1 = 16 + (0.46)(60)(5.92) = 179.5 \text{ Btu}; u_2 = 16 + (0.46)(10)(21.25) = 113.8 \text{ Btu}$$

$$\frac{({}_1W_2)_{\max}}{J} = u_1 - u_2 = 179.5 - 113.8 = 65.7 \text{ Btu}$$

$$\frac{{}_1W_3}{J} = (0.9)(65.7) = 59.1 \text{ Btu}; u_3 = u_1 - \frac{{}_1W_3}{J} = 179.5 - 59.1 = 120.4 \text{ Btu}$$

$$u_3 = 120.4 = 16 + (0.46)(10)v_3 \text{ or } v_3 = \frac{120.4 - 16}{(0.46)(10)} = 22.7 \text{ ft}^3$$

$$T_3 = \frac{p_3 v_3}{C} = \frac{(10)(22.7)}{0.37} = 613^\circ\text{R, or } 153^\circ\text{F}$$

As a result of irreversibility the final temperature increases from 114 to 153°F.

(b) The change of entropy during a reversible adiabatic process is zero. Therefore  $s_2 = s_1$  and  $s_3 - s_1 = s_3 - s_2$ . A constant-pressure process connects state 3 with state 2, and the change of entropy is



$$s_3 - s_1 = s_2 - s_2 = Mc_p \log_e \frac{T_3}{T_2} = (1)(0.238) \log_e \frac{613}{574} = (0.238)(0.0676) \\ = 0.0161 \quad [\text{Eq. (6:11) and Ex. 2:9}]$$

**6:4. The Enthalpy-Entropy (Mollier) Chart and the Steady-flow Process.** In actual engineering applications of thermodynamic principles steady-flow conditions are often closely approached. Important examples are the heat exchanger and the prime mover that were analyzed as steady-flow devices in Chap. 3. As was brought out in that chapter, the change of enthalpy during the steady-flow process is of special interest and significance, and the enthalpy-entropy diagram (often called the Mollier chart in honor of Richard Mollier, who first suggested it) is a useful tool in connection with steady-flow analyses. Charts of this type are available for most pure substances of engineering significance, specific values of the enthalpy (the enthalpy of unit weight) being plotted as ordinates against the values of the entropy of unit weight as abscissas.

A general  $hs$  chart is presented in Fig. 6:9. A steady-flow heat exchanger operates ideally at constant pressure, and it would therefore be convenient to have lines of constant pressure shown on the diagram. For the constant-pressure reversible process it has been shown in Art. 2:8 that  $dH$  may replace  $\partial Q$ . Thus  $ds = dh/T$  (constant pressure) and  $(dh/ds)_p = T$ . But  $(dh/ds)_p$  is the slope of a line connecting states having equal pressures on the Mollier diagram, and a typical constant-pressure line on the enthalpy-entropy diagram will have somewhat the appearance of line 1-2 of Fig. 6:9, increasing in slope in proportion to the increase of absolute temperature.<sup>1</sup>

Other lines, such as those connecting states of equal temperature, are also plotted on the Mollier diagram, and it is easily possible by using them to locate any given state of the substance as a point on the diagram. Thus, in the case of the steady-flow heat exchanger, points representing the state of the fluid at entrance and at exit from that unit may be located on the chart, the corresponding enthalpies read from the diagram, and the heat flow that has taken place during passage through the heat exchanger calculated as the difference of these enthalpies [see Eq. (3:9)].

<sup>1</sup> In the case of a two-phase mixture heat may be added simultaneously at constant pressure and at constant temperature (see footnote, p. 98). For the two-phase mixture the line of constant pressure on the Mollier chart would have a constant slope and therefore would be a straight line rather than a curve.

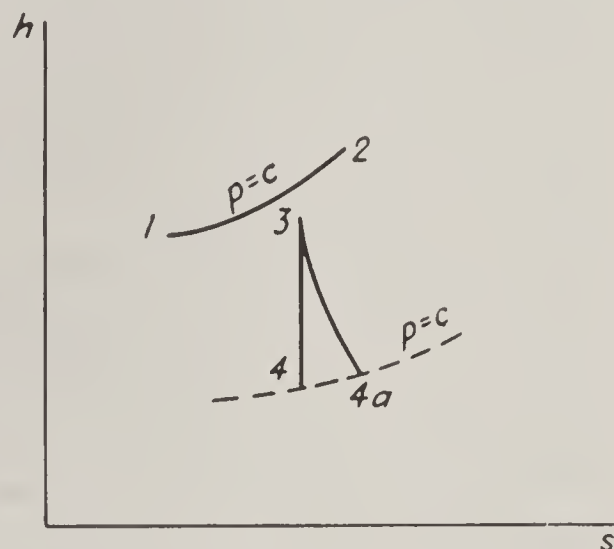


FIG. 6:9. The Mollier chart.

The process that takes place in the prime mover of the power plant is typically steady-flow and adiabatic. If idealized as a reversible process, it would be represented by a vertical line on the Mollier chart (see line 3-4 of Fig. 6:9). When the state of the fluid at entrance to the prime mover is known and some one property other than the entropy (such as the exhaust pressure) is established with regard to the condition of the fluid at exit from that unit, the state of the fluid at exit may be located. Then the maximum work that may be developed per pound of fluid flow may be calculated as equal to the decrease of enthalpy which has taken place [see Eq. (3:10)].

When the steady-flow process as carried out in the prime mover, though adiabatic, is not reversible, the effect of that irreversibility is reflected in a bending of the path to the right (toward increasing entropies) as has already been shown. If the exit state may be established, as at 4a in Fig. 6:9, then the work per pound of fluid flow may again be calculated by applying Eq. (3:10) and is seen to be less than the maximum by the difference between the enthalpies corresponding to states 4a and 4. Conversely, when state 3 and the work per pound of fluid flow are known, point 4a may be located.

The pressure-volume and temperature-entropy diagrams are of maximum value for the illustration and demonstration of thermodynamic principles. When those principles are known and the time has come to apply them to the solution of the practical engineering problem, the enthalpy-entropy chart is found to be a tool which is excellently adapted to that purpose.

*Example 6:4.* Assume that the gas of Example 1:10 approaches a steady-flow adiabatic prime mover at a pressure of 60 psia and a temperature of 500°F. In the prime mover, which, as has been shown in Chap. 3, may be either a turbine or (for quasi-steady flow) a reciprocating engine, an expansion takes place to a final pressure of 10 psia as in Example 6:3. Neglect differences in velocity and elevation at entrance and exit. (a) Assume the expansion to be reversible, and calculate the enthalpies at the initial and final states and the work per pound of gas expanded. (b) If irreversible and the condition of the gas at exit corresponds to state 3 of Example 6:3, calculate  $h_3$  and the work per pound of gas expanded. (c) Compare the work obtained from the steady-flow prime mover with the corresponding results of Example 6:3, and explain the differences.

*Solution:*

(a)  $p_1 = 60$  psia;  $T_1 = 960^\circ\text{R}$ ;  $v_1 = 5.92$  ft<sup>3</sup>;  $h_1 = 16 + (0.645)(60)(5.92) = 245.2$  Btu;  $p_2 = 10$  psia;  $T_2 = 574^\circ\text{R}$ ;  $v_2 = 21.25$  ft<sup>3</sup>;  $h_2 = 16 + (0.645)(10)(21.25) = 153$  Btu.

$$\frac{(1W_2)_{\text{steady flow}}}{J} = h_1 - h_2 = 245.2 - 153 = 92.2 \text{ Btu/lb}$$

(b)  $p_3 = 10$  psia;  $T_3 = 613^\circ\text{R}$ ;  $v_3 = 22.7$  ft<sup>3</sup>;  $h_3 = 16 + (0.645)(10)(22.7) = 162.3$  Btu.

$$\frac{(1W_3)_{\text{steady flow}}}{J} = h_1 - h_3 = 245.2 - 162.3 = 82.9 \text{ Btu/lb}$$

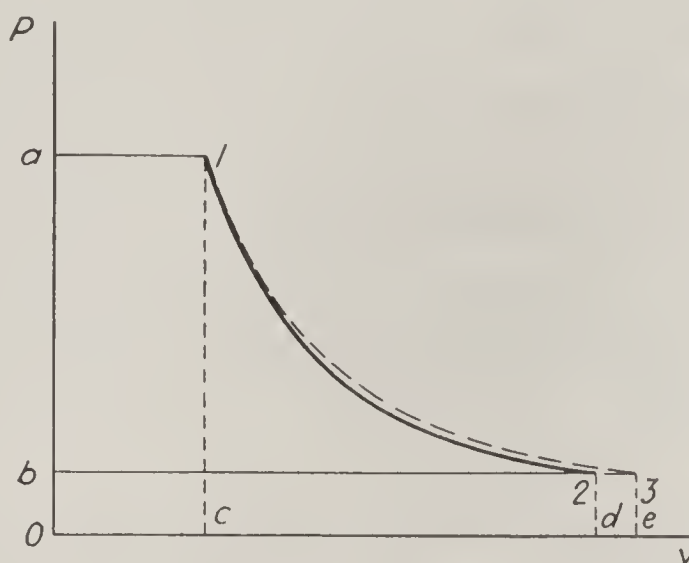


(c) Comparing the result of part *a* above with that of part *a* of Example 6:3, it is observed that the work obtained from the expansion of 1 lb of the gas in the reversible steady-flow turbine or engine is 92.2 Btu instead of 65.7 Btu as calculated in Example 6:3. If the device is a turbine, this difference is readily explained (see Chap. 3) as the difference between the flow work done *on* the open system at entry to the turbine and that done *by* the system at exit, or

$$\frac{P_1 v_1}{J} - \frac{P_2 v_2}{J} = \left( \frac{144}{778} \right) [(60)(5.92) - (10)(21.25)] = 26.5 \text{ Btu/lb}$$

Thus  $65.7 + 26.5 = 92.2$  Btu.

In the case of the engine, the work that accompanies the reversible adiabatic expansion *alone* is 65.7 Btu. It is represented by the area 1-2-*d*-*c* under the reversible process 1-2 of the figure which accompanies this example. But the engine operates continuously, and therefore the fluid system must follow some sort of cycle of events



that will eventually return it to state 1. If the pressure is steady at entrance and exit, the ideal cycle will be represented by 1-2-*b*-*a* of the figure. In this cycle the line *a*-1 represents the induction of the charge into the cylinder while the valve on the supply line is open. During this induction, work is performed on the piston equivalent to area *a*-1-*c*-0, or  $P_1 v_1$ . Similarly, line 2-*b* represents the rejection of the charge into the exhaust line. Area 2-*b*-0-*d* (a *negative* area) is the work done by the system on the piston during the process; this area is  $-P_2 v_2$ . Area 1-2-*d*-*c* has been shown to be  $J(u_1 - u_2) = J(65.7)$  ft-lb. No work is done on the piston while it is stationary during the process *ba*. Thus the net work of the cycle is

$$J(u_1 - u_2) + P_1 v_1 - P_2 v_2 = J(h_1 - h_2) \text{ ft-lb, or } 92.2 \text{ Btu/lb}$$

Note that *the engine and the turbine deliver the same maximum amount of work under equivalent supply and exhaust conditions*. The choice of a prime mover must be based on practical factors to be suggested later.

Now let us turn to the cycle that includes the irreversible expansion which is represented by the dashed line 1-3 of the figure. The area 1-3-*e*-*c* under this curve does not represent the work of expansion in this case because the process is irreversible and the net work of cycle 1-3-*b*-*a* cannot be calculated through the summation of areas as before. However, all other processes included in the cycle are reversible, and the areas beneath their paths therefore represent the work amounts that accompany them. The work performed as the result of irreversible process 1-3 *alone* has been shown to be  $u_1 - u_3 = 179.5 - 120.4 = 59.1$  Btu in Example 6:3. Adding the work (in Btu)

equivalent to area  $a-1-c-0$  and subtracting that represented by the area  $b-3-a-0$ , we have for the net work of the cycle

$$u_1 - u_3 + \frac{P_1 v_1}{J} - \frac{P_3 v_3}{J} = h_1 - h_3 \text{ (Btu) or } 59.1 + \frac{(144)(60)(5.92)}{778} - \frac{(144)(10)(22.7)}{778} = 82.9 \text{ Btu}$$

as in part *b* above.

**6:5. The Temperature-Entropy Diagram and the Reversible Cycle.** In Figure 6:10 is shown a Carnot (reversible) cycle plotted on  $TS$  coordinates. The heat supplied per cycle from the source at  $T_s(Q_s)$  is represented by the area beneath line 1-2 (area 1-2- $b$ - $a$ ) and the heat rejected to the refrigerator at  $T_R(Q_R)$  by the area 3-4- $a$ - $b$  under line 3-4. By difference the net work of the cycle is the enclosed area 1-2-3-4. But the efficiency of the reversible Carnot engine that operates on this cycle is the proportion which this net work bears to  $Q_s$ , or  $\frac{\text{area 1-2-3-4}}{\text{area 1-2-}b\text{-}a}$ , and a visual comparison of these areas makes it possible to estimate that efficiency without carrying out a detailed calculation. The same principle can be used to compare the efficiencies of all reversible cycles easily and effectively whether or not they, like the Carnot, receive and reject heat at constant temperature.

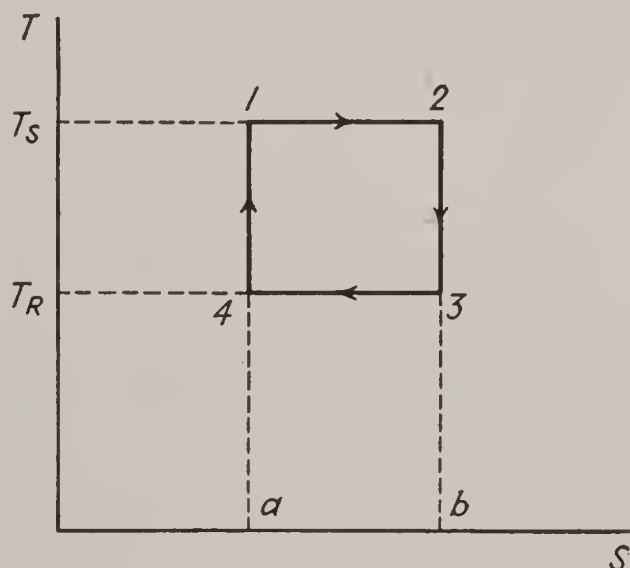


FIG. 6:10. The Carnot cycle on  $TS$  coordinates.

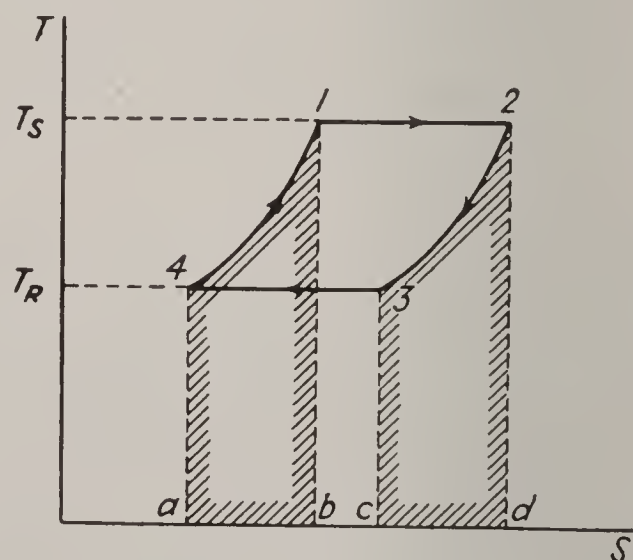


FIG. 6:11. The Stirling cycle on  $TS$  coordinates.

When regeneration is employed in the course of the cycle, it must be taken into account in making a visual estimate of the cycle efficiency. In Fig. 6:11 a Stirling cycle is pictured which is equivalent to the Carnot cycle of Fig. 6:10 in that it receives heat from the source at the same constant temperature  $T_s$  and rejects heat to the refrigerator at the same constant temperature  $T_R$ . These two processes are, however, connected not by adiabatics as for the Carnot but by constant-volume regenerative processes (see Art. 4:10). The crosshatched area 2-3- $c$ - $d$  represents heat rejected to the regenerator and eventually restored during process 4-1



(area 4-1-b-a); these heat quantities are neither discharged to the refrigerator at  $T_R$  nor accepted from the source at  $T_S$  and therefore do not form a part of  $Q_R$  or  $Q_S$ . Further, it may be shown by applying Eq. (6:10) that these areas are equal in size.  $Q_S$  is drawn from the source during process 1-2 and is represented by the area 1-2-d-b; if  $T_S$  is the same temperature in Figs. 6:10 and 6:11 and if the change of entropy  $S_2 - S_1$  is also the same in both cycles,  $Q_S$  for the Stirling cycle will equal  $Q_S$  for the Carnot cycle. Similarly, if  $T_R$  is the same temperature for both cycles, the area 3-4-a-c representing  $Q_R$  for the Stirling cycle can be shown to be equal to area 3-4-a-b of Fig. 6:10 and thus to  $Q_R$  for the Carnot since  $S_3 - S_4 = S_2 - S_1$  for both cycles. The cycle efficiencies will be equal as has already been demonstrated. If regeneration had not been brought into play, the efficiency of the cycle of Fig. 6:11 would have been less than that of the Carnot as an examination of the proportions of the two cycles on the  $TS$  diagram will show.

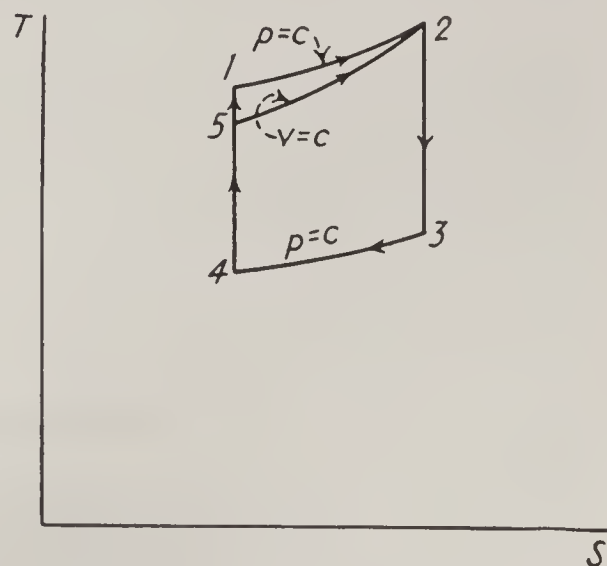


FIG. 6:12. Comparison of cycles on  $TS$  coordinates.

Let us consider and compare the two reversible cycles that are plotted together on the temperature-entropy diagram of Fig. 6:12. Both have the same maximum temperature of source and the same minimum temperature of refrigerator. Applying the suggestion made earlier in this article, it is observed that the efficiency of cycle 1-2-3-4 is greater than that of cycle 5-2-3-4 and that the reason it has this advantage lies in the higher average temperature at which heat is supplied from the source. Another observation is that the efficiency of both cycles would have been increased if the temperature  $T_2$  had been higher. A similar gain in efficiency would have resulted from a lowering of point 3. It is an accepted principle in thermodynamics that the atmosphere forms the standard refrigerator of the power cycle and therefore the temperature of the atmosphere is the lowest temperature at which heat may be rejected to the sink. Assuming  $T_4$  to represent the temperature of the atmosphere, if the constant-pressure process 3-4 could have been an isothermal at  $T_4$ ,  $Q_R$  would be reduced and the efficiency of both cycles would have been improved. For maximum cycle efficiency:

1. Heat should be supplied from the source at the highest average temperature that is practicable.
2. Heat should be rejected to the refrigerator at the lowest average temperature which is consistent with the practical situation.

**6:6. Entropy as a Criterion of Stability.** Stability is the characteristic of a system that measures its ability to resist changes in its state. It is always possible to change the state of a system by allowing it to exchange energy with its surroundings. For that reason stability is customarily evaluated with reference to a system isolated from its surroundings. For a system so situated  $\partial Q$  would be zero, and reference to Eq. (6:7) indicates that the entropy of the system could increase or, for the limiting (reversible) process, remain constant. If the entropy increased, that increase must have resulted from an irreversible process and the isolated system could not return to its original state. When, as the result of such irreversible changes, a state is attained at which the entropy is a maximum and no further change in state (except a reversible change) is possible, the system is said to be in *stable* equilibrium. From the First Law comes the statement:

*The stored energy of an isolated system will remain constant.* Based on the Second Law, it may be further stated:

*The entropy of an isolated system may increase but cannot decrease.* The latter statement is known as the *principle of the increase of entropy*. When combined with the statement based on the First Law, the result may be expressed as follows:

*Of all states at which the stored energy of the system is the same, the most stable is that corresponding to the greatest entropy.*

For the simple system, *internal energy* may replace *stored energy* in the preceding statement.

**6:7. Internal Irreversibility.** The irreversible processes that were the subject of discussion in Art. 6:3 were examples of *external irreversibility* in that the effects of the factors that cause irreversibility (friction, unrestrained expansion, and the flow of heat across a finite temperature interval) were in evidence at the boundaries of the system. But it has been brought out that even the isolated system may undergo an irreversible process during which its entropy will increase. This is classified as *internal irreversibility*. Whenever the various parts of a system are not at uniform temperature or uniform pressure, an irreversible internal change may be expected to result if the necessary disturbance is supplied.

Consider a continuous system that has been in contact at various sections of its boundary with external systems at different temperatures. As a result the temperature of the system is not uniform. If the external systems are removed, the system becomes an isolated system. Its state cannot be plotted as a single point on the temperature-entropy diagram, but it may be divided into many small systems each of which has a uniform temperature and each of which is therefore in an equilibrium state. The states of these infinitesimal subdivisions of the entire system will not persist, however, for the effects of molecular activity will be such as



eventually to equalize their temperatures. The process is not reversible since the external systems must again be called on to restore the original temperature differentials and the entropy of the system must have increased while it was isolated. The change of entropy may be calculated if sufficient information is available.

*Example 6:7A.* A system consists of a block of copper (specific heat 0.0915), weighing 200 lb and having a temperature of 200°F, and a bucket containing 100 lb of water (specific heat unity) at a temperature of 60°F. What change of entropy will result when the copper is immersed in the water? Neglect radiation and the thermal capacity of the bucket.

*Solution.* The internal energy of the system does not change. The energy exchanged between the copper and water is

$$(200)(0.0915)(200 - t) = (100)(1)(t - 60) \text{ or } t = 81.6^\circ\text{F}$$

in which  $t$  is the final temperature of both the copper and the water. The change of entropy of the copper is

$$(200)(0.0915) \log_e (541.6/660) = (200)(0.0915)(-0.198) = -3.62$$

The change of entropy of the water is

$$(100)(1) \log_e (541.6/520) = (100)(0.0412) = 4.12$$

The change of entropy of the entire system is

$$-3.62 + 4.12 = 0.5$$

*Example 6:7B.* A system consists of one pound of a gas with equations of state as in Example 1:10 at a pressure of 60 psia and a temperature of 200°F and a second pound of the same substance at the same pressure but at a temperature of 60°F. The system is confined within a rigid nonconducting container, the two parts being separated by a thin but rigid partition through which thermal energy passes until the temperatures of the two parts of the system are equalized. (a) At the end of this process, what has been the change of entropy of the system? (b) If, after the temperature has been equalized, the partition is punctured, will any further change of entropy result?

*Solution:*

(a) The final temperature of both parts of the system will be  $(200 + 60)/2 = 130^\circ\text{F}$ . The specific heat at constant volume for this gas is 0.17 (see Example 2:7), and the change of entropy for the system is

$$(1)(0.17) \log_e \frac{590}{660} + (1)(0.17) \log_e \frac{590}{520} = (0.17)(-0.0675 + 0.1267) = 0.0101$$

(b) At the end of the first process and before the partition is punctured, the pressures of the two parts of the system are unequal. The pressure of the part originally at higher temperature is  $(590)(60)/660 = 53.7$  psia (its volume has remained constant). Similarly, the pressure of the second part is  $(590)(60)/520 = 68.1$  psia. After the partition was punctured, these pressures were equalized at 60 psia while the temperature remained at 130°F. At this common pressure and temperature the system would have been in stable equilibrium even if the two parts had still been separated by the partition. We may therefore calculate the change of entropy during this second process as if the partition had not been punctured but had moved along the cylinder

as a piston might move; as a result of this movement the part at higher pressure would expand isothermally, and that at lower pressure would be compressed isothermally until their pressures were equalized. Equation (1:6) indicates that for these isothermal processes the product  $pv$  would not change and that therefore, by Eq. (1:7), there would be no change of internal energy of either part. Then, by Eq. (2:5),  $\partial Q = \partial W/J = P dV/J$ . But  $pv$  is constant, and  $P = 144p_1v_1/v = 144CT_1/v$ . Then

$$\Delta s = \int_1^2 \frac{\partial Q}{T} = \int_1^2 \frac{P dv}{JT} = \frac{144CT}{778T} \int_{v_1}^{v_2} \frac{dv}{v} = 0.185C \log_e \frac{v_2}{v_1} = 0.185C \log_e \frac{p_1}{p_2}$$

Applying this equation to each of the two parts of the system, the total change of entropy is

$$(0.185)(0.37) [\log_e (60/53.7) + \log_e (60/68.1)] = 0.0685(-0.1115 + 0.1269) = +0.00105$$

The total change of entropy as the two parts of the system are brought into temperature and pressure equilibrium is  $0.0101 + 0.00105 = 0.01115$ .

**6:8. The Availability and Unavailability of Heat.** It has been shown that not all of the heat taken from a source may be continuously changed to work, that the device which will change the maximum proportion of heat so received into work is the reversible engine of which the Carnot engine is an outstanding example, and that the proportion changed into work by the Carnot engine will depend on the temperatures of the source and of the refrigerator. It has also been brought out that the temperature of the refrigerator is, ultimately, that of the atmosphere and may therefore be considered a constant temperature. If the source is capable of supplying heat at constant temperature, the *maximum* portion of the heat it supplies that can be converted into work, as the result of a cyclic process with heat rejection to the atmosphere, may be readily calculated as the ratio of area 1-2-3-4 of Fig. 6:10 to area 1-2-*b*-*a* of the same figure. In thermodynamics this is called the *available* portion of the heat supplied by the source. Similarly, the ratio of area 4-3-*b*-*a* to area 1-2-*b*-*a* of the figure is that portion of the heat supplied by the source which not even the ideal Carnot engine could transform into work and is thus the *minimum* portion that must be rejected to the atmosphere (the refrigerator); this is termed the *unavailable* portion.

It has been inferred above that the source was infinite in extent and thus capable of supplying heat at constant temperature over an indefinite period of time. But it may be possible for even a finite system to act as a source in supplying heat at temperatures above that of the atmosphere, although, being finite in extent, such systems often change in temperature as they receive or emit heat. Suppose path 1-2 of Fig. 6:13 to represent a reversible process during which the system receives heat as its temperature changes. A small increment of heat produces only an infinitesimal temperature change and, as shown in the figure, can supply a small Carnot engine that rejects heat to the atmosphere at  $T_0$ . When the effects of all



these little Carnot cycles are combined, it is evident that the total heat they have constructively received is  $\int_1^2 T dS$  and is represented by the area 1-2-d-c under the path. This heat which has been received by the system is divided into two parts. The upper area 1-2-b-a is the sum of the enclosed areas of the Carnot cycles and represents the maximum work that could be produced from this heat as the result of a cyclic process; it is that part which is available. The lower area a-b-d-c, or  $T_0(S_2 - S_1)$ , is the sum of the heat amounts rejected to the atmosphere by the Carnot cycles and represents the minimum amount of heat that would be rejected to the atmosphere as work is developed due to a cyclic process; it is that part which is unavailable. Thus the available part of the total heat flow is  $\int_1^2 T dS - T_0(S_2 - S_1)$ , and the unavailable portion is  $T_0(S_2 - S_1)$ .

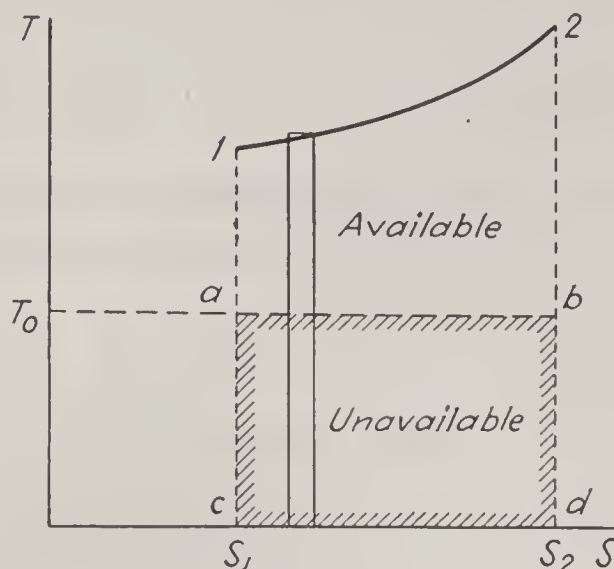


FIG. 6:13. Availability of heat-finite source.

**Example 6:8A.** One thousand Btu of heat leaves the hot gases in a boiler firebox at a constant temperature of 2000°F and enters the water in the boiler, evaporating it into steam at a constant temperature of 400°F. The temperature of the atmosphere is 80°F. (a) What is the change of entropy of the hot gases? (b) Of the water? (c) What part of the total heat that leaves the hot gases is available? What part is unavailable? (d) Divide the heat that enters the water into available and unavailable portions. (e) Considering the hot gases and the water to constitute a single system, calculate the change of entropy of this system as the result of the transfer of thermal energy between its parts, and compare the product  $T_0(S_2 - S_1)$  with the change of unavailable energy as calculated in (c) and (d) above.

**Solution:**

$$(a) \Delta S (\text{gases}) = -\frac{1000}{2460} = -0.406$$

$$(b) \Delta S (\text{water}) = \frac{1000}{860} = 1.162$$

$$(c) \text{Available portion (gases)} = 1000 \left( \frac{T - T_0}{T} \right) = 1000 \left( \frac{2460 - 540}{2460} \right) = 780 \text{ Btu}$$

$$\text{Unavailable portion (gases)} = 1000 - 780 = 220 \text{ Btu}$$

$$(d) \text{Available portion (water)} = 1000 \left( \frac{860 - 540}{860} \right) = 372 \text{ Btu}$$

$$\text{Unavailable portion (water)} = 1000 - 372 = 628 \text{ Btu}$$

$$(e) \Delta S = -0.406 + 1.162 = +0.756; T_0(S_2 - S_1) = (540)(0.756) = 408 \text{ Btu}$$

This agrees with the change of unavailable energy from (c) and (d) since  $628 - 220 = 408$  Btu.

**Example 6:8B.** One pound of the gas of Example 1:10 changes at constant pressure of 60 psia from  $t_1 = 200^\circ\text{F}$  to  $t_2 = 600^\circ\text{F}$ . The temperature of the atmosphere is 60°F. (a) Assuming the process to be reversible, what is the heat flow? (b) What part of this heat is available? Unavailable?

*Solution:*

$$c_p = 0.238$$

[Ex. 2:9]

$$(a) \quad {}_1Q_2 = Mc_p(t_2 - t_1) = (1)(0.238)(600 - 200) = 95.2 \text{ Btu}$$

$$(b) \quad s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} = 0.238 \log_e \frac{1060}{660} = (0.238)(0.474) = 0.113$$

$$\text{Unavailable portion} = T_0(s_2 - s_1) = (520)(0.113) = 58.7 \text{ Btu}$$

$$\text{Available portion} = 95.2 - 58.7 = 36.5 \text{ Btu}$$

**6:9. The psi function**, also called the Helmholtz free-energy function, is a composite and extensive property of the system that is defined by the expression

$$\Psi = E - TS \quad (6:12)$$

For the *simple system*,  $E = U$ , and we may write

$$\Psi = U - TS \quad (6:13)$$

or, for unit weight,

$$\psi = u - Ts \quad (6:14)$$

Maximum work is always associated with the reversible process. When the simple system undergoes an isothermal and reversible process, the *decrease* of the psi function is

$$\Psi_1 - \Psi_2 = U_1 - U_2 - T(S_1 - S_2) = -\Delta U + T \Delta S \quad (6:15)$$

But we may also write for this process

$$\frac{({}_1W_2)_{\max}}{J} = -\Delta U + ({}_1Q_2)_{\max} = -\Delta U + T \Delta S = \Psi_1 - \Psi_2 \quad (6:16)$$

It is observed that *the decrease of  $\Psi$  will measure the maximum possible work that can be performed by the system when the process takes place at constant temperature.*

If the system exchanges heat only with the atmosphere, the maximum value that  ${}_1Q_2$  may have is  $T_0(S_2 - S_1)$ . Returning to Eq. (2:3),

$$\begin{aligned} \frac{({}_1W_2)_{\max}}{J} &= U_1 - U_2 + ({}_1Q_2)_{\max} = U_1 - U_2 + T_0(S_2 - S_1) \\ &= (U_1 - T_0S_1) - (U_2 - T_0S_2) \\ &= \Psi_1 - \Psi_2 \end{aligned} \quad (6:17)$$

We may therefore conclude that *the decrease in the value of  $\Psi$  for the system between any two states in each of which it is in temperature equilibrium with the atmosphere will measure the maximum work that the system can produce during any process which connects those states provided that heat can be exchanged only with the atmosphere.* That this statement is valid may be shown by a return directly to the Second Law. For if a process that connects end states as described above and during which the system would produce an amount of work greater than  $\Psi_1 - \Psi_2$  could be found, then a



cycle could be formed by returning the system to the original state over a reversible isothermal path and net work could be developed at the expense only of energy taken from a single reservoir at uniform temperature.

**6:10. The zeta property**, or Gibbs free-energy function, is defined as

$$Z = E + \frac{PV}{J} - TS \quad (6:18)$$

When energy storage due to motion, gravity, capillarity, magnetism, and electricity is negligible, this may be rewritten as

$$Z = U + \frac{PV}{J} - TS = H - TS \quad (6:19)$$

or, for unit weight,

$$\zeta = u + \frac{Pv}{J} - Ts = h - Ts \quad (6:20)$$

The zeta function has much the same relation to the open system and the steady-flow process as has the psi function to the closed system and the nonflow process. Work that is done on the surroundings, such as the net flow work performed by the open system at points of entry and exit, was differentiated (see Chap. 3) from the useful work associated with the flow process. The amount of the corresponding deduction from the gross work is, for steady flow,  $P_2v_2 - P_1v_1$  per pound of fluid passing the boundaries. The decrease of  $\zeta$  is

$$\begin{aligned} \zeta_1 - \zeta_2 &= e_1 - e_2 + \frac{P_1v_1}{J} - \frac{P_2v_2}{J} - (T_1s_1 - T_2s_2) \\ &= \psi_1 - \psi_2 - \frac{P_2v_2 - P_1v_1}{J} \end{aligned} \quad (6:21)$$

The preceding article has made it clear that  $\psi_1 - \psi_2$  measures the maximum work that can be produced by the closed system of unit weight during a process which proceeds at constant temperature. When an open system and a steady-flow process (also at constant temperature) are involved, the maximum *useful* work that may develop can be found by deducting the net flow work from this gross amount. An examination of Eq. (6:21) will show that the right side of the equation indicates just such a deduction. We may therefore state that *the decrease in the value of  $\zeta$  will measure the maximum useful work per pound of fluid flow that can result from a steady-flow constant-temperature process which connects the states at which  $\zeta$  is measured.*

For an open system to be in equilibrium with the atmosphere, it is required that at points of entry and exit both the temperature *and the pressure* shall correspond with atmospheric temperature and pressure.

Substituting  $T_0$  for  $T_1$  and  $T_2$  and replacing  $P_1$  and  $P_2$  by  $P_0$ , Eq. (6:21) becomes

$$\zeta_1 - \zeta_2 = e_1 - e_2 + \frac{P_0(v_1 - v_2)}{J} - T_0(s_1 - s_2) \quad (6:22)$$

This equation states the maximum useful work that could be developed as the result of a constant-temperature process connecting states in each of which the system is in temperature and pressure equilibrium with the atmosphere. But, returning to the Second Law as in Art. 6:9, it becomes clear that this maximum applies also to *any* process which connects those states if there has been no heat exchange except with the atmosphere. Thus *the decrease in the value of  $Z$  between any two states in each of which it is in temperature and pressure equilibrium with the atmosphere will measure the maximum useful work that the system may produce during any process which connects those states provided that heat may be exchanged only with the atmosphere.*

Although the concept of the open system has been employed in its development, the foregoing principle is valid for the closed system also. For the work done on the atmosphere must be deducted from the total work to obtain the useful work; this deduction is  $P_0(V_2 - V_1)$ , and comparison will show that it is equivalent to the addition of the second term on the right side of Eq. (6:22).

The zeta function finds its most useful applications when chemical changes take place in the course of the contemplated process and the system consequently cannot be treated as composed of a pure substance. This explains why the more general term  $e$  replaces  $u$  in Eqs. (6:21) and (6:22). An example of its use is in connection with an analysis of the performance of an internal-combustion engine. The maximum work that can be delivered to the piston is equal to the decrease of  $Z$  between the original state of the mixture of fuel and air at the pressure and temperature of the atmosphere and the final state corresponding to pressure and temperature equilibrium of the products of combustion with the atmosphere. The zeta function finds numerous applications in the thermodynamics of chemistry.

When the system is the same pure substance at the beginning and end of the process,  $e_1$  and  $e_2$  in Eq. (6:22) may be replaced by  $u_1$  and  $u_2$ . In general, for that case, the internal energy, the volume, and the entropy are functions of  $p_0$  and  $T_0$ . Then  $u_1 = u_2 = u_0$ ,  $v_1 = v_2 = v_0$ ,  $s_1 = s_2 = s_0$ , and  $\zeta_1 = \zeta_2 = \zeta_0$ .\* This is called the *dead state*, since no useful work

\* It is assumed here that the storage of energy due to motion, gravity, capillarity, magnetism, and electricity is not necessarily absent but is negligible. An exception to the general case is found in two-phase mixtures for which the pressure and the temperature are not independent properties. For such mixtures the initial and final values of the internal energy, volume, and entropy need not be equal. But even in



may be obtained from the system. For the dead state

$$\zeta_0 = e_0 + \frac{P_0 v_0}{J} - T_0 s_0$$

Both the psi and the zeta properties may be compared with enthalpy in the sense that the change of a property measures the amount of a transitory quantity during a specified process. For it will be remembered that the change of enthalpy measured the heat flow during a constant-pressure nonflow reversible process and therefore the maximum heat flow, just as the decrease of psi and of zeta measures the maximum work that can accompany a constant-temperature process during a nonflow and a flow process, respectively. They differ from enthalpy, however, in that the concept of availability is introduced in both the decrease of psi and the decrease of zeta.

In addition to the uses specifically suggested above, the zeta function has great value as a basis for the evaluation of the maximum work that a system at any state may, in combination with an atmosphere at pressure  $p_0$  and temperature  $T_0$ , deliver for useful purposes to external systems. This application of the zeta function will be demonstrated in a later chapter.

### Problems

1. Which of the following statements are true? (a)  $\oint \frac{\partial Q}{T} = 0$  for a reversible cycle. (b)  $\oint \frac{\partial Q}{T} = 0$  for any cycle. (c)  $\oint dS = 0$  for a reversible cycle. (d)  $\oint dS = 0$  for any cycle.

2. In Art. 1:8, two simple cycles were described, both following the same state path. For the first,  $\oint \partial W = 0$ ; for the second  $\oint \partial W < 0$ . Determine, for each cycle, whether  $\oint \frac{\partial Q}{T}$  is equal to, greater than, or less than zero; also, whether  $\oint dS$  is equal to, greater than, or less than zero.

3. During a reversible process that takes place at a constant temperature of 300°F, 300 Btu of heat flows into a fluid system. (a) What is  $\int \partial Q/T$  for this process? (b) What is  $\int dS$ ? The same state path may be followed if the system is stirred while adding only 200 Btu of heat. For this second process, (c) what is  $\int \partial Q/T$ ? (d) What is  $\int dS$ ?

4. Work Example 6:1C, but substitute (a) gas W; (b) gas X; (c) gas Z. Are the changes of entropy the same for all four gases?

5. One pound of (a) gas W, (b) gas X, (c) gas Y, (d) gas Z changes from a state in which its pressure is 100 psia and its temperature is 400°F to a second state in which these properties are 80 psia and 300°F. Choosing any convenient reversible path, calculate the change of entropy. Check your answers by making a similar computation over some other reversible path that connects the same end states.

6. In tables that present the properties of water and steam, the entropy is shown as zero for liquid water at 32°F and a pressure of 0.088 psia. The specific entropy of

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this case  $\zeta_1 = \zeta_2 = \zeta_0$  since it will be found that the first two terms of Eq. (6:22) will be balanced by the last term and the right side of that equation will still be zero.

steam at the same temperature and pressure is tabulated as 2.1877. What qualification applies to the tabulation of this value as the entropy? Assuming that it is possible to find a reversible isothermal process which connects the two states, what heat flow will take place in the course of that process? Could the same change in state be accomplished by a process that is accompanied by a different heat flow than you have calculated above? Could the same change of state be accompanied by a different change in entropy than is shown in the tables?

7. Liquid water at 32°F and 0.088 psia (see Prob. 6) may be changed reversibly to liquid water at 212°F, 14.7 psia, during a process for which the heat-flow rate is very nearly constant at 1 Btu/lb for each °F increase in temperature. What is the tabulated value of the entropy for liquid water at 212°F, 14.7 psia?

8. When plotted on an absolute temperature vs. entropy diagram, the area under the state path (between the path and the  $S$  axis) of a certain reversible process, during which there is a continuous decrease in system entropy, is 3.1 in.<sup>2</sup> The scale of temperatures on the diagram is 1 in. = 200°R, and the scale of entropy is 1 in. = 0.4 rank. What heat flow accompanies the process? If the process took place at an average temperature of 240°F, what is the difference between the initial and final entropies of the system?

9. A reversible process, during which there is a continuous increase in system entropy amounting, in total, to 0.3 rank, is plotted on a temperature-entropy diagram for which the origin is located at 0°F. The area between the state path and the  $S$  axis is 2.4 in.<sup>2</sup> The scale of ordinates is 1 in. = 100°F and, of abscissas, 1 in. = 0.5 rank. What is the heat flow during the process?

10. In Example 2:10, what is the change of entropy of the system?

11. During an isothermal process, the entropy of a system composed of an ideal gas increases by 0.3 rank. The process takes place at 200°F. What maximum work may accompany the process? If the system had not been composed of an ideal gas, would the solution of this problem have been possible? Could the maximum heat flow have been calculated in both cases?

12. A certain adiabatic process takes place at constant internal energy. Based on Eq. (6:7) and (6:9), does the volume of the system increase or decrease?

13. At a certain state, a gas system has a pressure of 100 psia, a volume of 1 ft<sup>3</sup>, and a temperature of 400°F. Find the volume and temperature corresponding to a state having the same entropy but a pressure of 40 psia, if the system is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

14. Find the change of entropy for a 1-lb gas system as the result of a constant-volume process during which its pressure is halved if the system is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

15. A system is composed of a substance having a constant specific heat at constant volume of 0.4 Btu/(°F)(lb). Its entropy increases by 0.2 rank, its temperature from 50 to 200°F, during a constant-volume process. What is its weight?

16. Find the change of entropy of a 3-lb gas system during a constant-pressure process which doubles its volume if the system is composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ ; (d) gas  $Z$ .

17. The state path followed by a system during a certain constant-volume process is plotted on an absolute temperature-entropy diagram, and the area between the path and the  $S$  axis is found to be equivalent to 80 Btu. The heat flow during the process is 70 Btu. Which of the following statements are justified? (a) The change of internal energy of the system is 80 Btu. (b) The change of internal energy is 70 Btu. (c) During the process the internal energy increased. (d) The heat flow was negative. (e) The statement of the problem is a contradiction of thermodynamic principles.



18. The state path followed during an irreversible constant-pressure process is plotted on an absolute temperature-entropy diagram. Which of the following statements are true? (a) The area between the state path and the  $S$  axis is proportional to the heat flow. (b) The area is proportional to the change of enthalpy of the system. (c) If the entropy decreased during the process, the enthalpy must necessarily have decreased.

19. Work Example 6:3, but use a 1-lb system composed of (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ .

20. Show that, for an ideal gas, a line representing a constant-temperature change of state would be a horizontal line on the Mollier diagram.

21. The pressure and temperature of a gas is 100 psia and 400°F as it enters an adiabatic steady-flow expansion to a pressure of 20 psia, during which its entropy increases by 0.03 rank/lb. Assuming negligible differences in velocity and elevation at entrance and exit, calculate the external work performed per pound of gas flow if the gas is (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Y$ .

22. A gas approaches a steady-flow adiabatic prime mover at a pressure of 75 psia and a temperature of 500°F. The gas leaves the prime mover at a pressure of 15 psia. There are negligible differences between the velocities and the elevations at entrance and exit. The work performed is 10 per cent less than the maximum possible in adiabatic steady-flow expansion between the initial state and the final pressure. What is the final temperature if the gas is (a) gas  $W$ ; (b) gas  $X$ ; (c) gas  $Z$ ? What are the differences between the specific entropy at entrance and at exit for each of the gases?

23. A reversible closed-system cycle, when plotted on temperature-entropy coordinates, encloses an area of 2.5 in.<sup>2</sup> The scale of temperatures is 1 in. = 250°F; the scale of entropies is 1 in. = 0.5 rank. What is the net heat flow for the cycle? The net work?

24. A reversible cycle of an ideal-gas system consists of the following four processes in the order given: (1) an adiabatic compression from 100 to 700°F; (2) a constant-volume process ending at 2000°F; (3) an adiabatic expansion to 730°F; (4) a constant-volume process to the starting point. Plot this cycle approximately to scale on a  $T$ 's chart, and estimate the cycle efficiency by a visual comparison of areas on the diagram.

25. The same as Prob. 24, except that the four reversible processes which, in the order given, constitute the cycle are (1) an adiabatic compression from 100 to 975°F; (2) a constant-pressure expansion to 2000°F; (3) an adiabatic expansion to 730°F; (4) a constant-volume process which returns the system to its starting point. Based on a visual inspection of the two diagrams, how does the efficiency of this cycle compare with the efficiency of the cycle of Prob. 24?

26. On the diagrams drawn in the course of the solution of Probs. 24 and 25 superimpose a Carnot cycle which is supplied with heat from a source at a temperature equal to the highest temperature at which heat is supplied in either of the two cycles and which rejects heat to a sink at a temperature equal to their lowest temperature. Estimate visually the efficiency of this Carnot cycle, and check by calculation. How does its efficiency compare with the efficiencies of the cycles of Probs. 24 and 25?

27. Prove, based on the principle of the increase of entropy and Eq. (6:8), that the constant-internal-energy process described in Art. 2:11 and illustrated in Fig. 2:7 can take place in one direction only.

28. A system consists of a 50-lb iron ball (specific heat = 0.101) at a temperature of 200°F and a 100-lb bath of water (specific heat = 1) at 60°F. The ball is immersed in the water, and the two reach a common temperature. The exchange of energy with external systems is negligible. Prove, based on the principle of the increase of entropy, that the process is irreversible.

29. A pound of liquid water (specific heat = 1) at 70°F is heated at constant atmospheric pressure (14.7 psia) to 212°F and is then evaporated into steam as 970.3 Btu of heat is added at constant temperature. The temperature of the atmosphere is 70°F. What fraction of the heat expended in increasing the temperature of the water is available? What fraction of the heat supplied in evaporating the water into steam is available? What is the total change of available energy of the system? Of unavailable energy?

30. In Prob. 28, what is the change of available energy of the system if the temperature of the atmosphere is 50°F? What is the change of unavailable energy?

### Symbols

$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$C$	a constant
$e$	stored energy of unit mass, in general
$E$	stored energy of a system in general
$h$	enthalpy of unit mass
$H$	enthalpy of a system
$J$	proportionality factor
$k$	a constant ratio
$M$	mass
$p$	pressure, psi
$P$	pressure, psf
$Q$	heat flow
$s$	entropy of unit mass
$S$	entropy of a system
$t$	scalar temperature
$T$	absolute temperature
$u$	internal energy of unit mass
$U$	internal energy of a system
$v$	volume of unit mass
$V$	volume of a system
$W$	work

### Greek Letters

$\zeta$	zeta, or Gibbs free-energy, property of a unit system
$Z$	zeta, or Gibbs free-energy, property of a system
$\psi$	psi, or Helmholtz free-energy, property of a unit system
$\Psi$	psi, or Helmholtz free-energy, property of a system

### Subscripts

$p$	constant pressure
$R$	refrigerator
$S$	source
$v$	constant volume



## CHAPTER 7

### THE PURE SUBSTANCE

**7:1. Phases of the Pure Substance.** All pure substances follow much the same behavior pattern in passing through their various phases. At relatively low temperatures they are characteristically solids, and as the temperature rises they melt, or fuse, to become liquids. Finally, still farther up the scale of temperature, they vaporize into gases or vapors. The temperatures at which these transitions take place are not, for a given substance, fixed and definite but are functions of the pressure. The melting and boiling temperatures of different substances differ so widely that we are accustomed to speaking of them as gases, as liquids, or as solids according to their phase under the conditions at which we usually observe them. Thus iron is thought of as a solid, mercury as a liquid, and oxygen as a gas because at usual atmospheric temperatures and pressures they are observed in these phases. Water, on the other hand, is a substance which we observe in all three of these phases. Because of this and since, as perhaps the most important of thermodynamic pure substances, the amount of research that has been centered on the determination of its properties over a wide pressure-temperature range is undoubtedly greater than for any other substance, water is a convenient substance on which to base our study of the behavior of pure substances in general.

Let us begin with water in its solid phase, or as *ice*, and let us assume that we are dealing with 1 lb at a temperature of 0°F and at standard atmospheric pressure. We may raise the temperature of this ice by adding heat to it, and if we can devise a method of measuring this heat, it will be found that approximately 16 Btu will have been supplied as the temperature increases to 32°F. Since the heat has been supplied at constant pressure, its amount measures the change of enthalpy of this unit weight of ice. The specific heat at constant pressure is therefore approximately 0.5 Btu/(lb)(°F).

It will be remembered that this temperature of 32 deg was one of the two anchor points on the Fahrenheit scale of temperature and was, specifically, the melting point of ice under 1 standard atmosphere. We therefore expect to find a change in phase taking place that will eventually convert all of the ice into the liquid form which we call water. This conversion takes place at the constant temperature of 32°F and requires that 144 Btu of heat be supplied to change the pound of ice completely to the

form of a liquid. Heat supplied under conditions such as this is often referred to as the *latent heat of fusion*, the word latent being used to indicate that the effect of the addition of this heat is not visible in terms of a change of temperature. The use of latent heat of fusion may be criticized from the thermodynamic standpoint since melting could have been accomplished by supplying energy in the form of work. It will be noted that the pressure was, by assumption, constant during the melting process and that this 144 Btu therefore represented the increase of enthalpy during fusion; a better thermodynamic designation would therefore be the *change of enthalpy during fusion* or simply the *enthalpy of fusion*.

By increasing the pressure acting on the surface of the ice and water, we could have decreased the temperature at which fusion took place. The rate of decrease of melting temperature with increase of pressure is quite small, but, by increasing the pressure to some 2000 atm (about 30,000 psia), the temperature of fusion can be lowered to a minimum value of about  $-8^{\circ}\text{F}$ . Above this pressure the ice assumes a different crystalline structure, and the melting point rises. This new form of ice may be classified as an entirely separate and distinct phase. Bridgman<sup>1</sup> has described a total of seven different solid phases of water and has demonstrated that fusion temperatures above  $180^{\circ}\text{F}$  are possible. The ice phase with which we are familiar is designated as ice I, the others, similarly, as ice II to ice VII. Of these, ice II cannot be made to change directly into the liquid phase.

Returning to the lower anchor point of the Fahrenheit scale and assuming that the pressure is again constant at 1 standard atmosphere as we supply heat to the pound of water that has resulted from the melting of the ice, we observe that the temperature will again rise as we add this heat until the upper anchor point of  $212^{\circ}\text{F}$  is reached. During the interval of  $180^{\circ}\text{F}$  we shall have supplied some 180 Btu, and the mean specific heat is therefore (very nearly) unity. As we add further heat quantities, no further change in temperature is immediately observed; instead the liquid boils and progressively changes its form to a gas. To accomplish the complete conversion at this temperature and pressure into 1 lb of the gas (*steam*, or *water vapor*) requires the addition of some 970.3 Btu. This is the *latent heat of evaporation*, or, more properly, the *enthalpy of vaporization* at this pressure and temperature. After the liquid has been completely converted into the gaseous phase, a further supply of heat will cause the temperature to resume its upward march and the fluid becomes a *superheated vapor*, or *gas*. A distinction is sometimes made between these terms based on the number of degrees of superheat, but no definite and distinct boundary exists between the superheated vapor and the gas, and the two terms are often used synonymously.

<sup>1</sup> *J. Franklin Inst.*, **177**, 315(1914); *J. Chem. Physics*, **5**, 964(1937).



It has been noted that the fusion temperature of ice is a function of the pressure applied on its surface. The same is true of the boiling temperature of water. If the pressure on its surface had been 100 psia, for instance, instead of 1 standard atmosphere, the temperature of the water would have risen to about  $327.8^{\circ}\text{F}$  before it began to boil. To raise its temperature to this level from  $32^{\circ}\text{F}$  would have required that some 298.4 Btu of heat be supplied to the pound of water. Evaporation from and at this temperature (and under a constant pressure of 100 psia) would have required 888.8 Btu, the enthalpy of vaporization under these new conditions; it will be noted that, though the investment of heat in the liquid has been greater than for evaporation at  $212^{\circ}\text{F}$ , the enthalpy of vaporization has decreased. Conversely, if the pressure were 5 psia, the boiling temperature would be  $162.2^{\circ}\text{F}$ , the enthalpy of the liquid 130.1 Btu, and the enthalpy of vaporization 1001.0 Btu/lb.

The observed trend toward the decrease of the enthalpy of vaporization with increased temperature and pressure is consistent and is characteristic of all pure substances. It reaches its logical end point when the enthalpy of vaporization becomes zero. For water this comes at a temperature of about  $705^{\circ}\text{F}$  and a corresponding pressure of about 3206 psia. This is the so-called *critical point*. At each temperature between the melting point and the critical point a combination of pressure and temperature may be found at which the liquid and the vapor phases may be in pressure and temperature equilibrium and mixtures of the two phases may therefore exist in such equilibrium. Above the critical temperature this is not possible. If mixtures of the two phases exist above the critical temperature, they cannot be in equilibrium and will persist only so long as it takes for energy transfers to change the liquid into the vapor, the vapor into the liquid, or to bring the entire mixture below the critical temperature. The statement is often made that the critical temperature is the highest temperature at which the substance may exist in the liquid phase. This is subject to some criticism, for, at some temperatures and pressures in excess of the critical values of these properties, the characteristics of the substance are such that there is some doubt as to whether it should be classified as liquid or as gas. In this "twilight zone" it is perhaps better to avoid the issue by applying the term fluid to the condition of the substance. It may be safely said that the critical temperature is the highest temperature at which mixtures of the liquid and vapor phases may be in equilibrium.

A vapor that is in pressure-temperature equilibrium with its liquid is called a *saturated vapor*, the liquid a *saturated liquid*. Mixtures of the two will have extensive properties that will be dependent on the proportions of the vapor and the liquid in the mixture. For such mixtures the pressure and temperature are not independent properties, and the state of the

mixture cannot be determined without knowledge concerning at least one additional property. This property is often the *quality*. Quality is defined as the proportion of the vapor in the mixture by weight or the weight of vapor contained in 1 lb of the mixture and is conventionally designated by the symbol  $x$ . Any extensive property of such mixtures is the sum of the corresponding properties of its parts so that the total value of the property for the mixture of unit total weight would be  $x$  times the value of the property for the saturated vapor at the specified temperature (or pressure, for the pressure establishes the temperature, and vice versa) plus  $(1 - x)$  times the specific value of the same property for the saturated liquid at that temperature.

It has been observed that for each saturation temperature up to the critical temperature there is a corresponding saturation pressure. As we move downward along the scale of saturation temperatures, we find that there is a corresponding decrease in saturation pressures. At 32°F we find that the saturation pressure for water is about 0.089 psia. But the fusion temperature for ice, it will be remembered, increases with lowered pressure and was 32°F at 14.7 psia, 1 standard atmosphere. At a pressure of 0.089 psia the fusion temperature is 32.02°F. The intersection of the line of fusion temperatures with the line of saturation temperatures is called a *triple point* because at the corresponding pressure of 0.089 psia and temperature of 32.02°F the solid, liquid, and vapor phases of water may coexist in equilibrium.

Below the triple-point temperature the liquid cannot be saturated, *i.e.*, cannot be in pressure-temperature equilibrium with the vapor. By increasing the pressure, equilibrium may be maintained at lower temperatures between the solid and the liquid, as we have already observed. Similarly, by *decreasing* the pressure below 0.089 psia it is possible to maintain equilibrium between the solid and the vapor phases so that mixtures of these two phases at a common temperature and pressure are possible. If heat is supplied at constant pressure and temperature to equilibrium mixtures of the solid and vapor at temperatures below the triple-point temperature, the solid will change progressively directly into the form of a vapor without passing through any intermediate liquid phase. The heat required to accomplish the change of unit weight of the solid into the vapor under these conditions is called the *heat of sublimation* or, better, the *enthalpy of sublimation*. When wet clothing is exposed to air well below freezing temperatures, it will be observed to freeze and then to dry directly from this condition without again becoming “wet.” This occurs when the air is “dry,” *i.e.*, contains little water vapor, and results because the pressure of the water vapor in the air is below 0.089 psia and is therefore in the sublimation range. The thermodynamic principles that are involved will be discussed in greater detail in a later chapter.



**7:2. The  $pvT$  Surface.** The pure substance, in the absence of motion, gravity, capillarity, magnetism, and electricity, has only two independent properties. Based upon known values of these two, a third property may be established that, in combination with the first two, will represent a point in a space which has the three properties as its coordinates. Pressure and specific volume are two of the primary properties and are independent of each other. It is logical to select the third of the primary properties as the dependent property for the purpose of plotting a series of points and so developing a surface that will represent the equilibrium states of the substance. In that case the resulting surface would be designated as the  $pvT$  surface.<sup>1</sup>

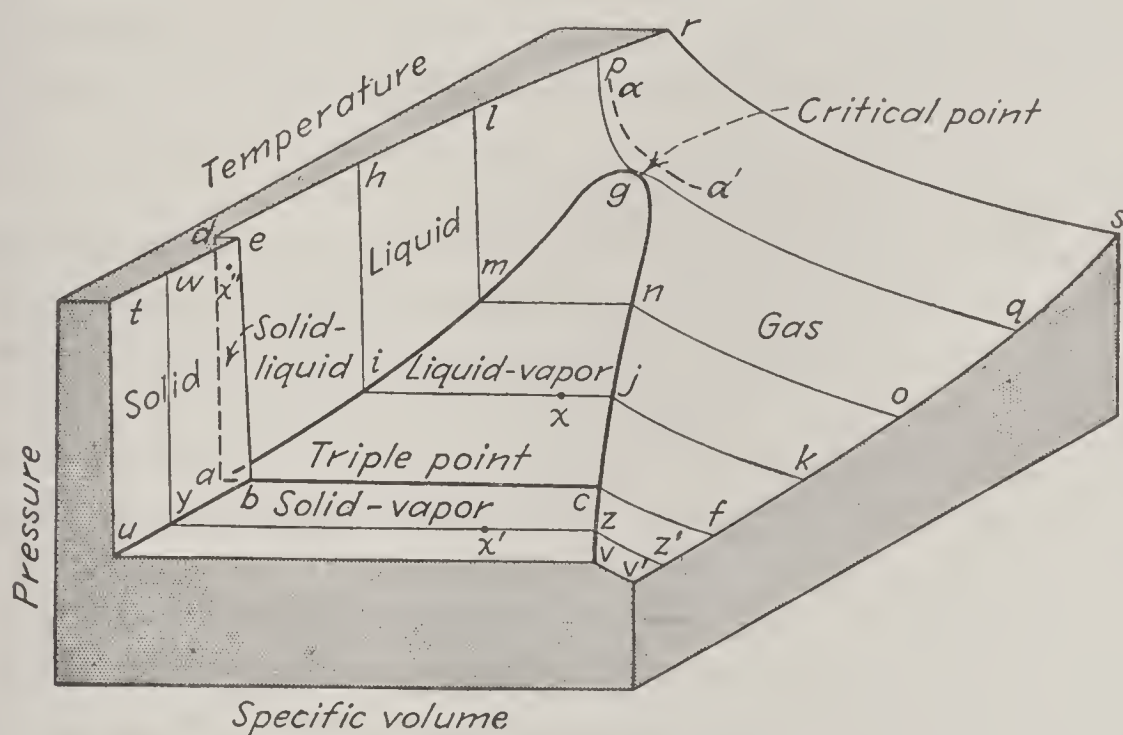


FIG. 7:1. The  $pvT$  surface for water (not to scale).

Figure 7:1 represents the  $pvT$  surface for the pure substance. It pictures the form of that surface for water in certain of its details but is not drawn to scale and is representative of the general characteristics of the surface for all pure substances. Referring to the notation of the diagram, the substance is at its triple point at any place along the line  $abc$ , a line of constant temperature and constant pressure corresponding to the values of these properties at the triple point. Points along this line correspond to various proportions of the three phases that can be in equilibrium at triple-point temperature and pressure. Point  $a$  represents (for water) the liquid phase alone and point  $c$  the vapor phase; point  $b$  might represent the solid phase alone, although it could also show the volume of a mixture

<sup>1</sup> Any three properties may be used for the delineation of a surface. For instance, when the internal energy, the absolute temperature, and the entropy are the space coordinates, the surface is called the  $uTs$ , or Gibbs, surface and finds use in discussions of relative stability and availability.

of liquid and vapor or of all three phases. This possibility will be examined in more detail in a later article.<sup>1</sup>

The line  $de$  is a line of constant temperature and pressure and shows the increase of volume as the water changes to ice at that pressure. For a substance that becomes less dense as it melts, point  $d$ , representing the liquid, would be to the right of  $e$ . The line  $eb$  is the locus of the increasing fusion temperatures of ice as the pressure is lowered; volumes along this line are those of the solid. Line  $da$  plots this same temperature increase for the liquid. For most substances the fusion temperature increases with increased pressure. The (concealed) surface  $deba$  is slightly curved toward increased temperatures at lower pressures for water but is perpendicular to the  $pT$  plane; points on this surface, such as  $x''$ , represent mixtures of the solid and liquid phases. For substances which expand as they melt this surface would not be concealed in the view shown in Fig. 7:1, and the curvature would be in the opposite direction, or toward decreased temperature at lower pressure.

The line  $aimg$  is the locus of the possible conditions of the saturated liquid,  $g$  being the critical point above which equilibrium mixtures of the liquid and vapor cannot exist. Similarly, the line  $cjng$  describes the locus of saturated vapor states. Lines  $mn$  and  $ij$ , crossing the space between these two curves, are lines of constant pressure and temperature and therefore normal to the  $pT$  plane. Points on this surface such as point  $x$  represent liquid-vapor mixtures in various proportions according to their locations; for example, point  $x$  may be estimated by its position to indicate a mixture of about 80 per cent vapor and 20 per cent liquid at the pressure and temperature corresponding to  $i$  (or  $j$ ). All possible liquid-vapor equilibrium states will lie on the surface outlined by the points  $aimgnjca$ . This surface curves upward to higher pressures at higher temperatures but is everywhere perpendicular to the  $pT$  plane.

Lines  $byu$  and  $czv$  are both plotted as the locus of sublimation pressures and sublimation temperatures, the first at the corresponding specific volume for the solid, the second for the vapor with which it is in equilibrium. Points along the constant-pressure constant-temperature line  $yz$  represent the volume of mixtures of the solid and the vapor that are in equilibrium at this pressure and temperature; for instance, the position of point  $x'$  indicates a proportion of about three-fourths vapor, one-fourth solid. The surface  $uybczvu$ , normal to the  $pT$  plane, includes equilibrium states for the solid-vapor mixture.

<sup>1</sup> The specific volume of water is less than that of ice. For most other substances the specific volume of the solid is less than that of the liquid, and point  $a$  would fall to the right of  $b$ . In that case, the position of point  $b$  on the surface could indicate the volume of unit weight of only the solid phase at the triple point while  $a$  could represent either all liquid or a mixture of phases.



As shown on the diagram, the phase borders are definite and distinct with the exception of that between the liquid and the gas near the critical point. The critical point  $g$  lies on both the saturated-liquid line and the saturated-vapor line. As the liquid passes this point, no change in any property is observed except that the fluid loses that property which is characteristic of a liquid and which we call surface tension. It will be remembered that surface tension enables a liquid to maintain a distinct boundary surface and, at points of contact with the vapor, to form a meniscus. The transition across point  $g$  has been observed experimentally. The only visual evidence of that transition is the disappearance of the meniscus. At this point the liquid does not "boil," in the sense that the change to the vapor phase is gradual; yet there is no abrupt change in volume, for the volumes of the liquid and vapor phases are equal. The change in phase is instantaneous, and mixtures of the two phases are not observed.

The line  $pgq$  is a line of constant temperature corresponding to the critical temperature. A point on the surface  $dhlpgmiad$  may be definitely classified as representing an equilibrium state of the liquid, and the line  $pg$  is accordingly often taken as being the boundary between the liquid and gas phases. The problem is not as simple as that, however, for a state such as that represented by  $\alpha$ , lying not too far above  $pg$ , may have characteristics which leave us in doubt as to whether it should be classified as liquid or gas. If the pressure is lowered without change of temperature, the path  $\alpha\alpha'$  will be followed. At  $\alpha'$  the substance has definitely assumed the characteristics of a gas; yet at every point during the transition the substance has remained homogeneous in phase composition, *i.e.*, there has been no mixture of phases. If  $\alpha$  is considered to be a liquid state, then the change to the gas phase has been, like that observed at the critical point, abrupt though not explosive. We shall adopt the policy of classifying states such as  $\alpha$  simply as *fluid* states and thus avoiding the issue.

Lines  $lmno$  and  $hijk$  are lines of respectively constant temperature that pass successively over the liquid surface, the two-phase liquid-vapor surface, and the gas surface. Because the liquid is compressible to only very slight degree,  $lm$  and  $hi$  are nearly vertical. Line  $pg$ , also a constant-temperature locus, deviates noticeably from the vertical; as the critical temperature is approached, the liquid becomes more compressible. The sections  $mn$  and  $ij$  across the liquid-vapor surface are normal to the  $pT$  plane, as has been observed previously. Segments  $no$  and  $jk$  of these constant-temperature lines are curves which, when projected on the  $pv$  plane, are approximate hyperbolas in shape. As we move to the right along these lines (toward lower pressures), the projection of the curve more and more becomes truly hyperbolic in shape. A reference to Eq.

(1:6), an equation of state for the so-called ideal gas, indicates that lines of constant temperature on the  $pv$  plane would, for that class of substances, be true hyperbolas. At pressures that are low relative to the critical pressure, the gas phase of any pure substance approaches the characteristics of the ideal gas.

The line  $wyzz'$ , also a constant-temperature line, crosses successively the surfaces that represent the solid, the solid-vapor mixture, and the

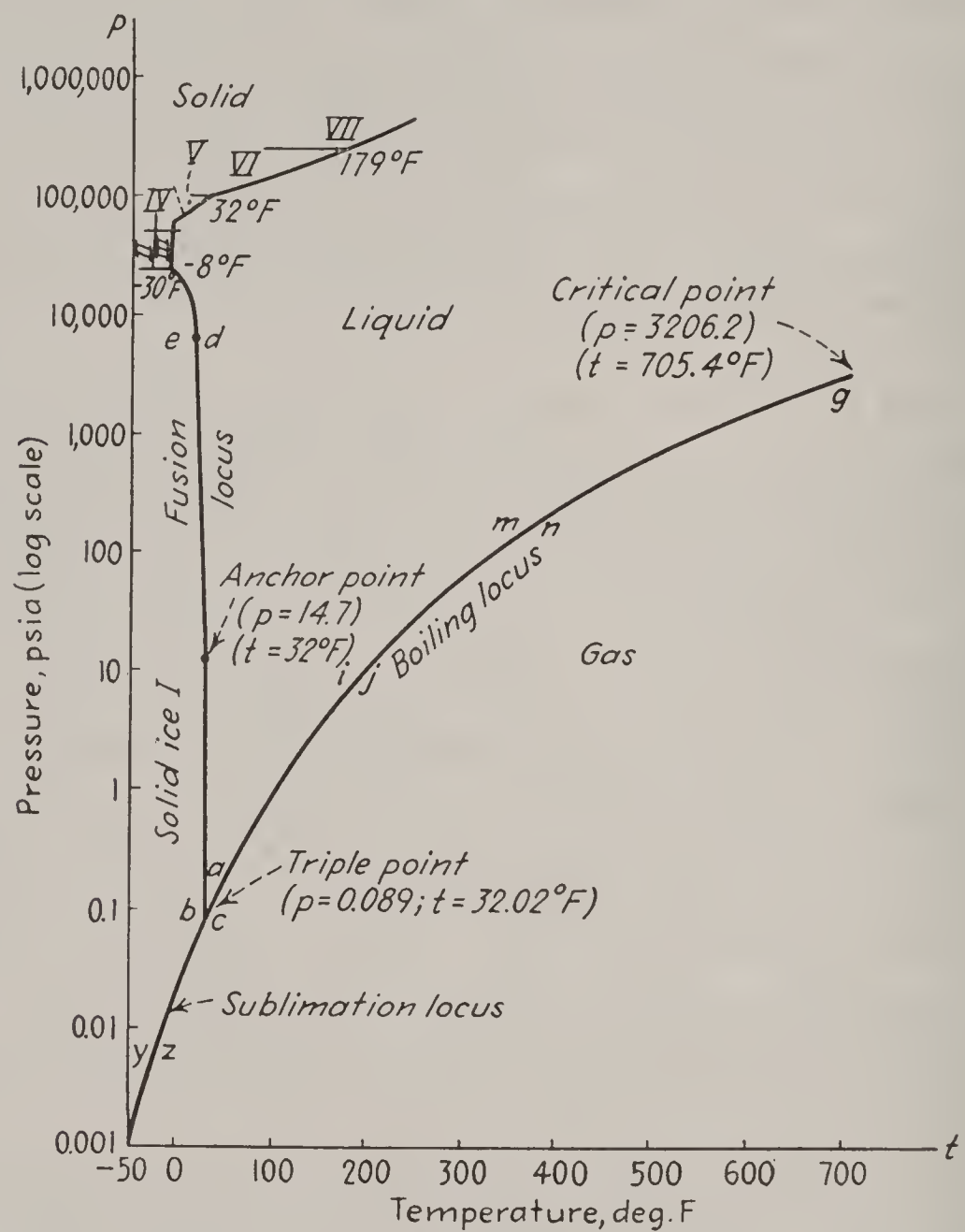


FIG. 7:2. Phase diagram for water.

vapor. The solid is even less susceptible to compression than the liquid, and  $wy$  is practically a vertical line. Segment  $yz$  is normal to the  $pT$  plane, of course, and  $zz'$ , because of the relatively low pressures along its entire length, projects on the  $pv$  plane as almost an exact hyperbola.

**7:3. The Phase Diagram.** Referring to Fig. 7:1, it will be noted that the surfaces which represent mixtures of two phases are everywhere perpendicular to the  $pT$  plane and will project as curved lines on that plane. The triple point is normal to the  $pT$  plane and will project as a point. The entire projection forms a pattern of connecting lines and is called a



*phase diagram.* Figure 7:2 illustrates a phase diagram for water; included are the lines that divide all seven of the solid phases of this pure substance. Because of the wide range of pressures that is covered, a logarithmic scale has been used for pressure. Within the range of Fig. 7:1, Fig. 7:2 is lettered to correspond with that figure.

The various solid phases of ice are distinguished by differences in crystalline structure. The lines that separate each phase from its neighbors have the same significance as the lines in the lower part of the figure

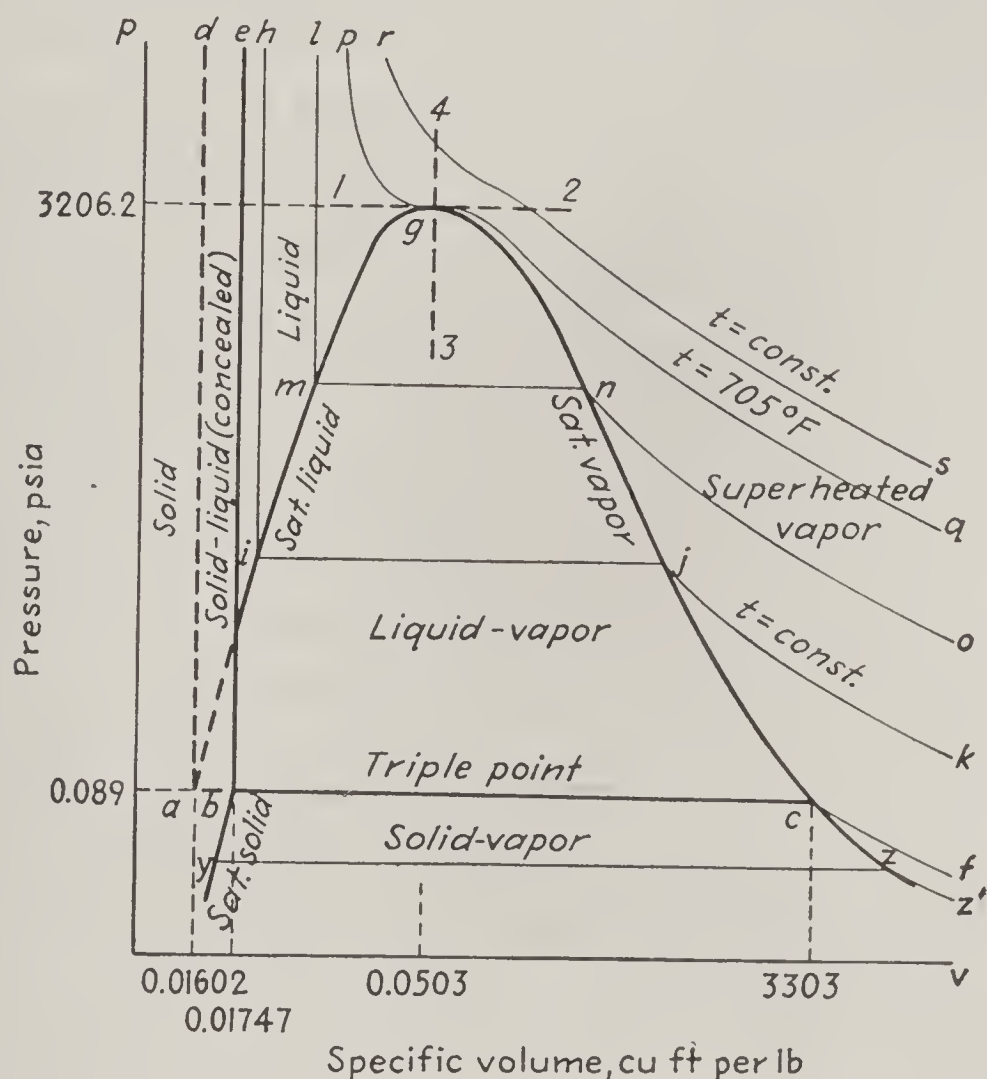


FIG. 7:3. Pressure-volume diagram for water (not to scale).

in that they designate pressure-temperature relationships under which mixtures of the two phases may exist in equilibrium. For instance, the common boundary of ice I and ice III is horizontal and extends between temperatures of about  $-30$  and  $-8^{\circ}\text{F}$ , indicating that equilibrium mixtures of these two phases may exist at only one pressure but over the designated range of temperature. The intersections of these lines may be classed as additional triple points since they designate the pressure and temperature at which three phases may coexist.

**7:4. The pressure-volume diagram** is obtained by projecting the lines that separate phases and phase mixtures on Fig. 7:1 to their positions on the  $pv$  plane. Figure 7:3 is a pressure-volume diagram for water on which the lower pressures and specific volumes have been greatly exaggerated

in order to prevent congestion at the left and near the bottom of the diagram; the figure is therefore not to scale, but, as a guide, the pressures at the triple point and the critical point and the corresponding volumes of the saturated liquid, solid, and vapor are shown on the coordinate axes. This diagram is also lettered to agree with Fig. 7:1. The triple point appears as a line since one of the coordinates is an extensive property. The liquid surface is partly concealed by the surface representing the compressed solid; it extends to the right from line  $da$ . The boundary between the liquid surface and the gas surface is somewhat indefinite, as explained in a preceding article, but falls approximately along the line  $pg$ . The increasing resemblance of the isothermals  $rs$ ,  $gq$ ,  $no$ ,  $cf$ , and  $zz'$  to

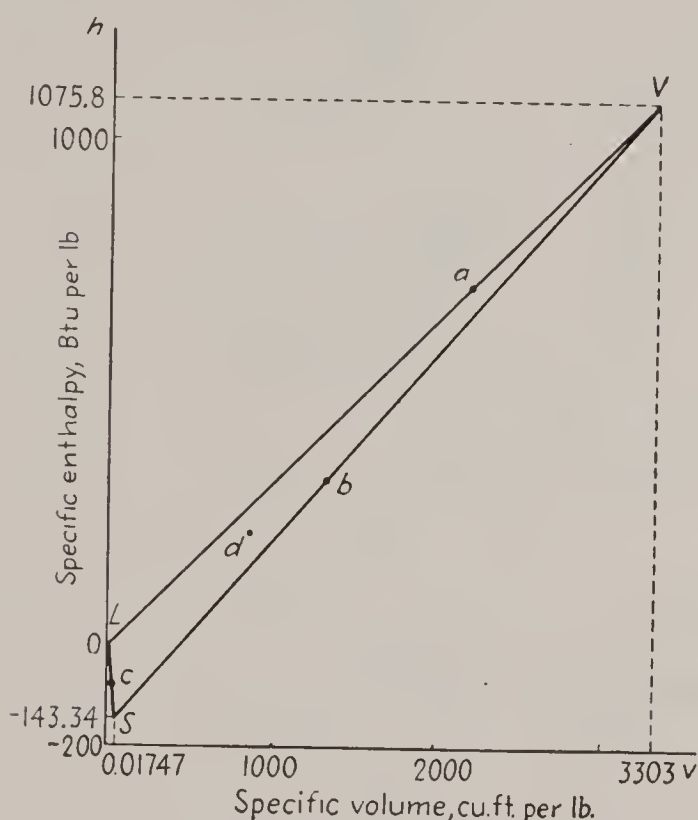


FIG. 7:4. The triple point (water).

hyperbolas in this projection as the pressure decreases below its value at the critical point is a significant feature of this diagram.

**7:5. The triple point** plots as a point on the pressure-temperature diagram. When one of these intensive properties is used in conjunction with an extensive property, such as volume (see Fig. 7:3), it becomes a line. In general, if extensive properties are measured along both coordinates, the triple point defines an area on the resulting diagram.<sup>1</sup> As shown in Fig. 7:3, at the triple point the specific volume of the solid is 0.01747 ft<sup>3</sup>, of the liquid 0.01602 ft<sup>3</sup>, and of the

vapor 3303 ft<sup>3</sup>. The corresponding *relative* values of the enthalpy, referred to an arbitrary base to be discussed later are, respectively, -143.3, 0.02, and 1075.8 Btu. The corresponding points are plotted as  $S$ ,  $L$ , and  $V$  on Fig. 7:4, an enthalpy-volume diagram. The volume of the solid and the liquid have been exaggerated on this chart, for clarity.

Any point on the line joining  $L$  and  $V$  in Fig. 7:4 (as point  $a$ ) represents a mixture of only the liquid and vapor phases at triple-point pressure and temperature. Similarly, point  $b$  denotes a mixture of the solid and the vapor and point  $c$  a mixture of liquid and solid in equilibrium at this pressure and temperature. The proportions of the two constituents in the mixture is indicated by the position of the point. For example, the position of point  $a$  indicates that the weight of vapor in unit weight of the

<sup>1</sup> An exception is the enthalpy-entropy, or Mollier, diagram.



liquid-vapor mixture is numerically equal to the ratio of the distance between  $L$  and  $a$  to that between  $L$  and  $V$ .

Any point (as point  $d$  of Fig. 7:4) that lies within the triangular triple-point area represents a mixture of all three phases. If the respective weights of the three phases in unit weight of the mixture are designated as  $x_s$ ,  $x_L$ , and  $x_v$  and the known values of the extensive properties used to define state  $d$  are  $p_1$  and  $p_2$ , a set of three simultaneous equations may be written, as follows:

$$\begin{aligned} p_1 &= x_s p_{1s} + x_L p_{1L} + x_v p_{1v}; & p_2 &= x_s p_{2s} + x_L p_{2L} + x_v p_{2v} \\ 1 &= x_s + x_L + x_v \end{aligned}$$

in which  $p_{1s}$ ,  $p_{1L}$ , and  $p_{1v}$  are, respectively, the known values of the first extensive property for 1 lb of the solid, the liquid, and the vapor and  $p_{2s}$ ,  $p_{2L}$ , and  $p_{2v}$  are the corresponding values of the second extensive property.

**7:6. The Critical Point.** If water under the critical pressure of 3206 psia and at a temperature below the critical temperature of 705°F enters a transparent tube and receives heat as it flows slowly through the tube, its temperature will progressively increase to the critical temperature. As it passes this temperature, it becomes a gas and, if further heat is supplied, continues to increase in temperature. This process is shown as line  $1g2$  in Fig. 7:3. The transition from liquid to gas is not readily observable, for surface tension is a property that gradually disappears, vanishing entirely at the critical point, and no well-defined meniscus will be apparent at temperatures close to the critical temperature, but if some substance that had a distinctly different color in the gas phase from that which distinguished the liquid were put through an equivalent process, the change in phase at the critical point would be found to be abrupt.

In order to observe the disappearance of the meniscus, let us assume that a mixture of the saturated liquid and the saturated vapor in exactly the right proportions is placed in a transparent container and heated. If the pressure and temperature originally are well below their values at the critical point, a distinct meniscus, or separation surface, will be apparent between the liquid and the vapor. As heat is added, the liquid will boil and the pressure and temperature will rise along the curve  $cjng$  of Fig. 7:2, maintaining equilibrium between the two phases. This boiling indicates that the proportion by weight of vapor in the mixture is increasing, but the meniscus will be observed to remain near the center of the container. This reflects the greater susceptibility of the vapor to compression and the characteristic of the liquid that causes it to reflect the effects of temperature rather than pressure in its volume changes. As the critical pressure and temperature are neared, the meniscus becomes less distinct and finally vanishes as the critical point is reached and passed. The process is illustrated as  $3g4$  in Fig. 7:3. If too large a proportion of the liquid had

been placed in the container originally, the meniscus would have risen during heating and would have reached the top before the critical pressure had been attained. If too little liquid had been introduced, the meniscus would have vanished at the bottom at a pressure less than the critical pressure.

**7:7. Tables of Properties.** When an equation of state connecting three properties of the pure substance is known, the values of other essential properties that correspond to a given state may be determined. Equation (1:6) is an example of the simplest possible equation of state, but it applies with adequate accuracy to only a small portion of the gas surface of Fig. 7:1. When the range of states in which interest is centered falls within the area to which this simple equation applies, we may, as has been shown in earlier chapters, calculate without too much difficulty the values (or, at least, the *relative* values) of certain other properties at various states of the substance. To cover the entire surface with sufficient accuracy, a series of equations much more complicated than Eq. (1:6) is often required, each covering a specific range and matching accurately at the borders of its area of application the results obtained for points along that border from another equation of state which has been designed to apply to the adjacent area. These equations are normally so complicated that a great amount of research and calculation has been directed toward the preparation and tabulation of continuous solutions for the equations of state for certain especially important substances. These tabulations give the values of the more essential properties over a wide range of states and are called *tables of properties*. Their form is more or less standardized, and they normally are keyed by pressure, temperature, or both, and give values of the volume, the enthalpy, and the entropy corresponding to states within the range to which they apply. The internal energy is sometimes included, at least over a part of the tabulated range, but may be obtained from the enthalpy, pressure, and volume by a simple calculation. One table, keyed by temperature, usually covers the saturation range, and a second, keyed by both pressure and temperature, is devoted to the gas or superheated vapor. In exceptional cases, additional tables are available for the compressed liquid or the solid.

The most complete, careful, and accurate investigations have concerned themselves with the properties of water and steam. Many steam tables have been published, each successive tabulation reflecting certain refinements in experimental or other method or covering a new range. Widely used in engineering calculations at present, "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes<sup>1</sup> is an example. The discussion to follow will be based on this tabulation. The solution of many of the problems included in this text will require that the reader make use

<sup>1</sup> John Wiley & Sons, Inc., New York, 1936.



of some standard steam table. The solution of the examples is based on the Keenan and Keyes tables wherever the properties of water and steam are concerned.

TABLE 7:1. SATURATION: TEMPERATURES\*

Temp., °F, <i>t</i>	Pres- sure, psia, <i>p</i>	Sp. volume			Enthalpy			Entropy		
		Sat. liquid <i>v<sub>f</sub></i>	Evap. <i>v<sub>fg</sub></i>	Sat. vapor <i>v<sub>g</sub></i>	Sat. liquid <i>h<sub>f</sub></i>	Evap. <i>h<sub>fg</sub></i>	Sat. vapor <i>h<sub>g</sub></i>	Sat. liquid <i>s<sub>f</sub></i>	Evap. <i>s<sub>fg</sub></i>	Sat. vapor <i>s<sub>g</sub></i>
326	97.52	0.01772	4.521	4.538	296.52	890.2	1186.7	0.4717	1.1330	1.6047
328	100.26	0.01774	4.403	4.421	298.60	888.6	1187.2	0.4743	1.1281	1.6024
330	103.06	0.01776	4.289	4.307	300.68	887.0	1187.7	0.4769	1.1233	1.6002

\* Abstracted by permission from Table 1, "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.

TABLE 7:2. SATURATION: PRESSURES\*

Pressure, psia, <i>p</i>	Temp., °F, <i>t</i>	Sp. volume		Enthalpy			Entropy			Internal energy		
		Sat. liquid <i>v<sub>f</sub></i>	Sat. vapor <i>v<sub>g</sub></i>	Sat. liquid <i>h<sub>f</sub></i>	Evap. <i>h<sub>fg</sub></i>	Sat. vapor <i>h<sub>g</sub></i>	Sat. liquid <i>s<sub>f</sub></i>	Evap. <i>s<sub>fg</sub></i>	Sat. vapor <i>s<sub>g</sub></i>	Sat. liquid <i>u<sub>f</sub></i>	Evap. <i>u<sub>fg</sub></i>	Sat. vapor <i>u<sub>g</sub></i>
98	326.35	0.01772	4.517	296.89	889.9	1186.8	0.4721	1.1322	1.6043	296.57	808.3	1104.9
99	327.08	0.01773	4.474	297.65	889.4	1187.0	0.4731	1.1304	1.6035	297.33	807.7	1105.0
100	327.81	0.01774	4.432	298.40	888.8	1187.2	0.4740	1.1286	1.6026	298.08	807.1	1105.2
101	328.53	0.01775	4.391	299.15	888.2	1187.4	0.4750	1.1268	1.6018	298.82	806.5	1105.3
102	329.25	0.01775	4.350	299.90	887.6	1187.5	0.4759	1.1251	1.6010	299.57	805.9	1105.4
103	329.96	0.01776	4.310	300.64	887.1	1187.7	0.4768	1.1234	1.6002	300.30	805.3	1105.6

\* Abstracted by permission from Table 2, "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.

Tables 1 and 2 of the Keenan and Keyes tables deal with the properties of the saturated liquid and the saturated vapor with which it may be in pressure-temperature equilibrium. Table 1 is keyed by temperatures (from 32 to 705.4°F, the critical temperature) and Table 2 by pressures (from a pressure of 0.25 in. Hg, or 0.123 psia, to an upper limit of 3206.2 psia, the critical pressure). Tables 7:1 and 7:2 are based on these tables.

It will be observed that Tables 7:1 and 7:2 cover approximately the same range of states and illustrate the convenience of two tables although either one alone would be adequate. If, for example, we are interested in saturated water, saturated steam, or a mixture of the two at a temperature of, say, 327.2°F, interpolation is much more simple and more rapidly performed if Table 1 is used; similarly, if the pressure is known, the use of Table 2 is indicated. Another convenience is the inclusion of tabulated

values of the internal energy in Table 2. This is not a usual feature of tables of properties because the internal energy may be easily computed from the enthalpy, pressure, and volume. Its inclusion requires some crowding and the omission of one of the columns of Table 1.

The tables are, to a considerable extent, self-explanatory. We are already familiar with the use of the symbols  $v$ ,  $h$ ,  $s$ , and  $u$  to denote specific values of the volume, enthalpy, entropy, and internal energy, respectively. The subscript  $f$  may be read as “of the saturated liquid,” the symbol  $g$  as “of the saturated vapor.” When the subscript  $fg$  appears, it denotes the difference between the values of that property for the saturated liquid and the saturated vapor or the *change* of the property as the liquid completely vaporizes at constant temperature and pressure. It may be read as “of evaporation”; for example,  $h_{fg}$  is the “enthalpy of evaporation.” Specific volumes are tabulated in cubic feet per pound, enthalpy and internal energy in Btu per pound, and the entropy in ranks per pound.

The values of the enthalpy, entropy, and internal energy are relative and are the differences between the values of these properties at the given state and at some state at which they are arbitrarily assigned a zero value. Enthalpy and entropy have a zero value for the saturated liquid at 32°F. Pressure and volume are measured in terms of their absolute values, and the internal energy of the saturated liquid at 32°F is therefore very slightly negative; the difference is so small that it has little practical significance. As a matter of technical accuracy, the choice of the saturated liquid at 32°F as the base level is somewhat inconsistent, for this temperature is slightly below the triple-point temperature and this substance cannot exist as a liquid at the combination of temperature and pressure as stated in the first line of Table 1 of the unabridged tables; it must be a vapor, a solid, or a mixture of these two phases. From the practical standpoint, a level that corresponds with the lower anchor point of the Fahrenheit scale of temperature has more convenience, and this outweighs the very slight inaccuracy that is involved.

Data taken from Table 1 or Table 2 may be applied to the calculation of the properties of an equilibrium mixture of the liquid and vapor phases. The pressure and temperature of such mixtures will, of course, correspond in accordance with the relationship presented in those tables regardless of the proportions of liquid and vapor. The value of any extensive property (volume, enthalpy, entropy, internal energy) is the sum of its values for the parts. The quality  $x$  denotes the weight of vapor in 1 lb of the mixture, and the weight of liquid is thus  $1 - x$ . We may therefore write

$$\begin{aligned} v &= (1 - x)v_f + xv_g \\ h &= (1 - x)h_f + xh_g \\ s &= (1 - x)s_f + xs_g \\ u &= (1 - x)u_f + xu_g \end{aligned} \tag{7:1}$$



in which  $v$ ,  $h$ ,  $s$ , and  $u$  are the values of the corresponding properties for 1 lb of the mixture of quality  $x$ . Taking into consideration the fact that  $v_g = v_f + v_{fg}$ , etc., each of these equations may be converted to the following two forms, which may be used according to relative convenience:

$$\begin{aligned} v &= v_f + xv_{fg} = v_g - (1 - x)v_{fg} \\ h &= h_f + xh_{fg} = h_g - (1 - x)h_{fg} \\ s &= s_f + xs_{fg} = s_g - (1 - x)s_{fg} \\ u &= u_f + xu_{fg} = u_g - (1 - x)u_{fg}. \end{aligned} \quad (7:2)$$

When Table 7:1 is used and the internal energy cannot be calculated directly from tabulated values, it may be obtained as  $u = h - 144pv/J$ . The specific volume of the liquid is usually so small as compared with that of the vapor that the volume of the former is often neglected, and, as an approximation,  $v = xv_g$ . This approximation may be used only in the case of the volume and becomes less accurate at low quality and at high temperatures and pressures.

*Example 7:7A.* Find the temperature and values of the specific volume, enthalpy, entropy, and internal energy for wet steam at a pressure of 85 psig and having a quality of 0.90 (90 per cent). Atmospheric pressure is 30.56 in. Hg.

*Solution.* The pressure of the atmosphere is  $(0.491)(30.56) = 15.0$  psia. Adding this to the gage pressure, the pressure of the steam is 100 psia. The corresponding saturation temperature is 327.81°F. This temperature will apply to *all* qualities at this pressure.

At high qualities the calculation of the values of the extensive properties is more easily and accurately made by using the second form of Eqs. (7:2). Thus

$$\begin{aligned} v &= v_g - (1 - x)v_{fg} = 4.432 - (1 - 0.9)(4.432 - 0.018) = 4.432 - 0.4414 = 3.991 \text{ ft}^3/\text{lb} \\ h &= h_g - (1 - x)h_{fg} = 1187.2 - (1 - 0.9)(888.8) = 1187.2 - 88.9 = 1098.3 \text{ Btu/lb} \\ s &= s_g - (1 - x)s_{fg} = 1.6026 - (1 - 0.9)(1.1286) = 1.6026 - 0.1129 = 1.4897 \\ u &= u_g - (1 - x)u_{fg} = 1105.2 - (1 - 0.9)(807.1) = 1105.2 - 80.7 = 1024.5 \text{ Btu/lb} \end{aligned}$$

Note that it is not appropriate to carry the calculation to a greater number of significant places than is presented in the tables.

The quality is high and the pressure moderate so that the approximation might have been applied in the calculation of specific volume. Checking,

$$v = xv_g = (0.90)(4.432) = 3.989 \text{ ft}^3/\text{lb}$$

The internal energy may alternately be calculated as

$$u = h - \frac{144pv}{J} = 1098.3 - \frac{(144)(100)(3.991)}{778} = 1098.3 - 73.8 = 1024.5 \text{ Btu/lb}$$

Table 3 of the Keenan and Keyes tables tabulates the properties of superheated steam in the form shown in Table 7:3.

Temperature and pressure are independent properties of the gas or superheated vapor and, in that range, may be used to establish all other properties of the pure substance. Table 3 is keyed by pressure and temperature and is most convenient for use when these two properties are

known. However, the table may be entered with any two of the tabulated properties (pressure, temperature, volume, enthalpy, entropy), and if the assigned values lie within the scope of the tabulation, systematic search will locate the corresponding state and, with it, the values of the other properties. The range of pressures covered by the table is from 1 psia to the critical pressure of 3206.2 psia, and the range of temperatures is from the saturation temperature corresponding to each pressure to 1600°F. The last portion of Table 3 in its unabridged form carries the pressures above the critical pressure to a maximum of 5500 psia. A part of the data in this section of the tabulation applies to the “twilight zone” to which reference has previously been made and even overlaps across line *pg* of Figs. 7:1 and 7:3 to encroach on the compressed-liquid surface.

TABLE 7:3. SUPERHEATED VAPOR\*

Pressure, psia (sat temp.)		Sat. liquid	Sat. vapor	Temperature, °F								
				330	340	350	360	370	380	390	400	420
99 (327.08)	<i>v</i>	0.018	4.474	4.496	4.569	4.641	4.712	4.783	4.852	4.921	4.989	5.124
	<i>h</i>	297.6	1187.0	1187.7	1194.6	1200.3	1205.9	1211.5	1217.0	1222.4	1227.7	1238.3
	<i>s</i>	0.4731	1.6035	1.6056	1.6130	1.6201	1.6271	1.6338	1.6403	1.6467	1.6530	1.6651
100 (327.81)	<i>v</i>	0.018	4.432	4.448	4.521	4.592	4.663	4.732	4.801	4.870	4.937	5.071
	<i>h</i>	298.4	1187.2	1188.5	1194.3	1200.1	1205.7	1211.3	1216.8	1222.2	1227.6	1238.1
	<i>s</i>	0.4740	1.6026	1.6043	1.6117	1.6188	1.6253	1.6325	1.6391	1.6455	1.6518	1.6639
102 (329.25)	<i>v</i>	0.018	4.350	4.355	4.427	4.497	4.567	4.635	4.703	4.770	4.836	4.968
	<i>h</i>	299.9	1187.5	1188.0	1193.9	1199.7	1205.3	1210.9	1216.4	1221.9	1227.3	1237.9
	<i>s</i>	0.4759	1.6010	1.6016	1.6090	1.6162	1.6232	1.6300	1.6366	1.6430	1.6493	1.6615

\* Abstracted by permission from Table 3, “Thermodynamic Properties of Steam” by J. H. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.

The units in which the various properties are measured are the same as in Tables 1 and 2. The internal energy is not tabulated but may be readily calculated as  $u = h - 144pv/J$ . Occasionally it is necessary to identify a state when one of the two known properties is the internal energy. Table 3 does not lend itself readily to this purpose but may be used by first locating the approximate area in the table that includes the required state by methods which will suggest themselves and then applying trial-and-error or graphical methods to locate the state more accurately. It will be noted that, grouped with the pressure along the left border of Table 3, data taken from Table 2 and covering the properties of the saturated liquid and vapor are tabulated. This will often be a convenience as when the calculation of the increase of a property during superheating at constant pressure is of interest.



*Example 7:7B.* Determine the specific volume, enthalpy, entropy, and internal energy of steam at a pressure of 100 psia and a temperature of 400°F. What is the mean specific heat at constant pressure? Compare it with the *instantaneous* value at 400°F. Refer to Fig. 6 of the Keenan and Keyes tables, and check.

*Solution.* The specific volume, enthalpy, and entropy are read directly from Table 3 and are, respectively, 4.937 ft<sup>3</sup>/lb, 1227.6 Btu/lb, and 1.6518. The internal energy may be calculated as

$$u = h - \frac{144pv}{J} = 1227.6 - \frac{(144)(100)(4.937)}{778} = 1227.6 - 91.3 = 1136.3 \text{ Btu/lb}$$

The mean, or average, specific heat at constant pressure is  $(\Delta h/\Delta t)_p$ . Starting from the saturated vapor at 100 psia, the increase of specific enthalpy has been 1227.6 – 1187.2 = 40.4 Btu and the increase of temperature 400 – 327.81 = 72.19°F. The mean specific heat at constant pressure,  $c_{pm} = (40.4/72.19) = 0.56$  Btu/(°F) (lb). The instantaneous specific heat,  $c_{pi}$ , may be determined with sufficient accuracy by calculating  $(\Delta h/\Delta t)_p$  over a range of temperatures for which 400°F is the mid-point. Table 3 makes it convenient to choose this interval as 380 to 420°F, and the change of temperature is therefore 40°F. The corresponding change of specific enthalpy is 1238.1 – 1216.8 = 21.3 Btu and  $c_{pi} = 21.3/40 = 0.532$  Btu/(°F) (lb). It is the instantaneous value of the specific heat that is plotted in Fig. 6 of the Keenan and Keyes tables, and our value, when spotted on that figure, seems in good agreement with the data which it presents.

TABLE 7:4. COMPRESSED LIQUID\*

Pressure, psia, (Sat. temp.)		Temp., °F						
		32	100	200	300	400	500	600
	Sat. liquid	$p$ 0.08854	0.9492	11.526	67.013	247.31	680.8	1542.9
		$v_f$ 0.016022	0.016132	0.016634	0.017449	0.018639	0.020432	0.023629
		$h_f$ 0	67.97	167.99	269.59	374.97	487.82	617.0
		$s_f$ 0	0.12948	0.29382	0.43694	0.56638	0.68871	0.8131
1000 (544.61)	$(v - v_f) \times 10^5$	−5.7	−5.1	−5.4	−6.9	−8.7	−6.4	
	$h - h_f$	+2.99	+2.70	+2.21	+1.75	+0.84	−0.14	
	$(s - s_f) \times 10^3$	+0.15	−0.53	−1.20	−1.64	−2.00	−1.41	
2000 (635.82)	$(v - v_f) \times 10^5$	−11.0	−9.9	−10.8	−13.8	−19.5	−27.8	−32.6
	$h - h_f$	+5.97	+5.31	+4.51	+3.64	+2.03	−0.38	−2.5
	$(s - s_f) \times 10^3$	+0.22	−1.18	−2.39	−3.42	−4.57	−5.58	−4.3

\* Abstracted by permission from Table 4, "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.

The properties of the compressed liquid are covered in Table 4 up to a pressure of 6000 psia. The liquid surface of Fig. 7:1 is covered up to that pressure with the exception of a small triangular area below 32°F, where the fusion temperature is slightly below 32°F because of the imposed pressure; the omission of this area is unimportant. Sample lines based on Table 4 are shown in Table 7:4.

Table 4 in its unabridged form carries the temperatures up to the

critical temperature of 705.4°F. Grouped with these temperatures at the top of the table are the corresponding saturation pressure and the values of the specific volume, enthalpy, and entropy for the saturated liquid. The increments of these properties, as the result of the application of a superpressure on the surface of the liquid, are small, and their values are accordingly stated, when the available information warrants that practice, to a larger number of significant places than in Table 1. In the lower part of the table, the increments of each of these properties that correspond to each superpressure are tabulated. These increments are applied as additions to or subtractions from the corresponding values for the saturated liquid and are arranged, for convenience, in a manner such that the last place of the increment corresponds with the last place shown in the tabulation at the head of the column. Thus at a pressure of 2000 psia and a temperature of 100°F the specific entropy of the compressed liquid is  $0.12948 - 0.00118 = 0.12830$ , while at the same pressure but at a temperature of 600°F the corresponding calculation is  $0.8131 - 0.0043 = 0.8088$ . Some time may be saved in the use of Table 4 by remembering and applying this feature.

A detailed examination of Table 4 reveals that the degree of compressibility of water increases at an accelerated rate as the critical temperature is approached. At 5000 psia the volume is less than the volume of the saturated liquid by less than 2 per cent at 32°F and by about 46 per cent at the critical temperature. Not so very many years ago very little quantitative information was generally available with respect to the compressibility of water, and it was customary to assume it to be incompressible in calculating the properties of the superpressure liquid. On the basis of that inaccurate assumption, if pressure were applied on the surface of the saturated liquid (with no heat flow), there would be no change in volume and thus no work would be in evidence and no energy would cross the boundaries of the liquid system. As a consequence, neither the internal energy nor the entropy could change, and the enthalpy of the superpressure liquid was necessarily greater than that of the saturated liquid at the same temperature. When compressibility is taken into account, the decrease in volume represents energy in the form of work that enters the system. As a result of the entry of this energy, the temperature of the liquid rises slightly, and, in order to return it to the reference level of temperature, heat must be taken from the system. This negative heat flow is accompanied by a decrease of entropy, as shown over the major portion of Table 4, and is also accompanied by a decrease of internal energy. When the degree of compressibility is small, as for temperatures up to about 400°F, the effect of this decrease of internal energy on the enthalpy is not large enough to cancel the increase of enthalpy that is caused by the higher pressure and the increment of enthalpy, with respect



to the enthalpy of the saturated liquid, is positive. At higher temperatures and correspondingly higher compressibility, this increment becomes negative. At 32°F it is noted that the increment of entropy is positive; this is due to the unusual characteristic of liquid water in having its greatest density not at the fusion temperature but a few degrees above that point.

*Example 7:7C.* A pump receives saturated water at a temperature of 200°F and discharges it continuously at a pressure of 1500 psia. If the compression is isentropic (adiabatic and reversible), calculate (a) the final temperature of the water and (b) the work required per pound of water pumped.

*Solution:*

(a) The state of the water at entrance will be designated by the subscript 1, that at exit from the pump as 2. Then, using Table 4,  $p_1 = 11.526$  psia;  $v_1 = 0.016634$  ft<sup>3</sup>/lb;  $h_1 = 167.99$  Btu/lb;  $s_1 = s_2 = 0.29382$ . At  $p_2 = 1500$  psia, the specific entropy of the compressed liquid is 0.29203 at 200°F, 0.43441 at 300°F. Interpolating between these limits, the temperature corresponding to  $s_2$  is found to be 201.25°F. An interpolation over so wide a range is, of course, subject to some criticism, and the final temperature might differ from our result by a few hundredths of a degree.

(b) At 1500 psia and 200°F, the specific enthalpy of compressed water is  $167.99 + 3.36 = 171.35$  Btu; at the same pressure and 300°F, it is 272.29 Btu. Interpolating for a temperature of 201.25°F,  $h_2$  is found to be 172.61 Btu. Applying the steady-flow energy equation [Eq. (3:5)] and neglecting differences in velocity and elevation at entrance and exit,  ${}_1W_2/J = h_1 - h_2 = 167.99 - 172.61 = -4.62$  Btu/lb.

Figure 3, located just below Table 4 in the Keenan and Keyes tables, is a convenience for the solution of problems of this character. Figure 3 is similar to a Mollier chart for the compressed liquid except that the *difference* between the enthalpies of the compressed and the saturated liquids is measured along the ordinate instead of the total enthalpy. Applying it to the solution of this problem, point 1 is located at the intersection of the line of constant temperature of 200°F with the bottom line of the diagram, which represents saturation states. Projecting vertically upward (at constant entropy) to the line representing the final pressure of 1500 psia, the results of our calculation are very closely checked in a fraction of the time required to carry out the detailed computation that is made above.

For the isentropic process,  $dh = v dP/J$  (see Example 3:6), and since the change in volume is minor, this provides an easy, if approximate, method of calculating the change of enthalpy as

$$\Delta h = \frac{v \Delta P}{J} = \frac{0.016634(1500 - 11.5)(144)}{778} = 4.57 \text{ Btu}$$

Table 5 presents the properties of the solid and the vapor in the upper portion of the temperature range in which a mixture of these two phases may be in temperature-pressure equilibrium. It is in much the same form as Table 1, being keyed by temperature. A few sample lines are presented in Table 7:5.

Table 5 requires little detailed explanation. The range of the unbridged table is from 32 down to -40°F. At the latter temperature the saturation pressure is 0.0019 psia. The subscript  $g$  has the same meaning

TABLE 7:5. SATURATION: SOLID-VAPOR\*

Tempera- ture, °F, <i>t</i>	Pressure, psia, <i>p</i>	Sp. volume		Enthalpy			Entropy			Internal energy		
		Sat. solid <i>v<sub>i</sub></i>	Sat. vapor <i>v<sub>g</sub></i> × 10 <sup>-3</sup>	Sat. solid <i>h<sub>i</sub></i>	Subl. <i>h<sub>ig</sub></i>	Sat. vapor <i>h<sub>g</sub></i>	Sat. solid <i>s<sub>i</sub></i>	Subl. <i>s<sub>ig</sub></i>	Sat. vapor <i>s<sub>g</sub></i>	Sat. solid <i>u<sub>i</sub></i>	Subl. <i>u<sub>ig</sub></i>	Sat. vapor <i>u<sub>g</sub></i>
32	0.0885	0.01747	3.306	-143.35	1219.1	1075.8	-0.2916	2.4793	2.1877	-143.35	1164.9	1021.6
20	0.0505	0.01745	5.658	-149.31	1219.9	1070.6	-0.3038	2.5425	2.2387	-149.31	1167.0	1017.7
10	0.0309	0.01744	9.05	-154.17	1220.4	1066.2	-0.3141	2.5977	2.2836	-154.17	1168.6	1014.4

\* Abstracted by permission from Table 5, "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.



as before. The subscript  $i$  may be read as “of the saturated solid,” and  $ig$  refers to the change of the property during sublimation. The same reference levels for the evaluation of enthalpy, entropy, and internal energy are, of course, retained.

Also included in the Keenan and Keyes tables are Table 6, giving the viscosity of saturated water and both saturated and superheated steam,

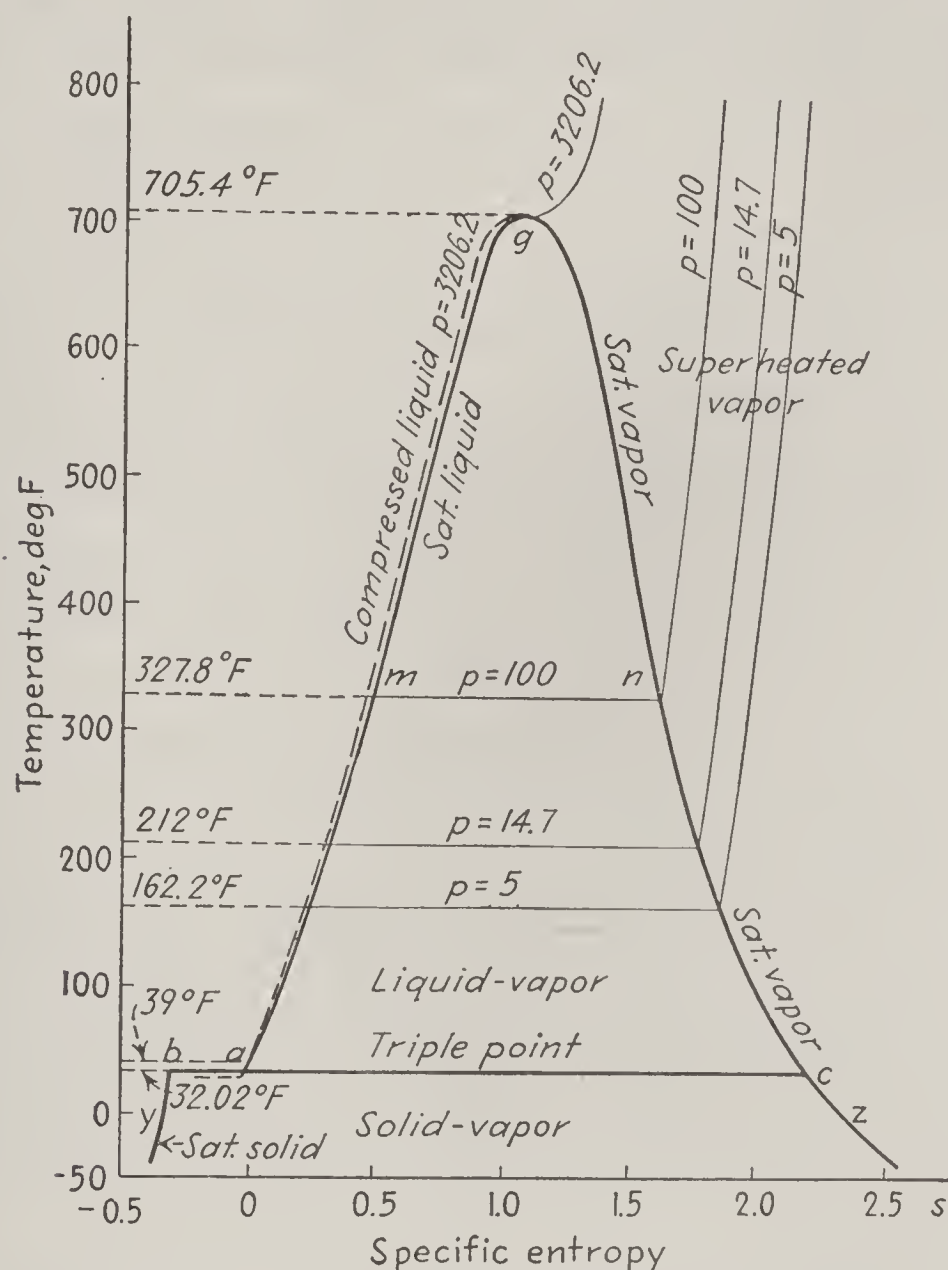


FIG. 7:5. Temperature-entropy diagram for water.

and Table 7, which tabulates the thermal conductivity of the saturated and superheated vapor.

**7:8. The Temperature-Entropy Diagram.** Figure 7:5 shows a temperature-specific entropy diagram for water. Saturated-liquid states have been plotted from steam-table values as the line  $ag$ , the saturated-vapor states as  $gcz$ . The line  $by$  is the locus of the states of the saturated solid. Between  $ag$  and  $gc$  lies the area that represents equilibrium mixtures of the liquid and the vapor, and mixtures of the solid and the vapor are located in the area below the triple-point line and between  $yb$  and  $cz$ . The superheated-vapor area lies to the right of  $gz$  and extends into the region above  $g$ . The compressed-liquid area lies close alongside the

line  $ag$  and to its left except below the temperature of greatest density of water ( $39^\circ\text{F}$ ), where it crosses to the right side of this line. The compressed-solid states, for which no quantitative data are available to us in the tables, lie closely along the left side of  $yb$ .

Lines of constant pressure of 100, 14.7, and 5 psia have been drawn across the liquid-vapor area of Fig. 7:5 and extended into the superheated-vapor region. If the chart were extended downward to a temperature of absolute zero ( $-460^\circ\text{F}$ ), the area under these lines, as was brought out in Chap. 6, would be equal to the change of enthalpy between the states which they connect. Thus the area under  $mn$  would be  $h_{fg}$  at 100 psia, or 888.8 Btu. This area is rectangular and easily measured as the product of its height, or the saturation temperature in degrees Rankine, and its width, the change of entropy during evaporation,  $s_{fg}$ ; thus  $h_{fg} = T_{\text{sat}}s_{fg}$ . Similarly, the area under a line of constant pressure in the superheated-vapor region will measure changes of enthalpy between points on that line. This area is less readily calculated but equals, of course,  $\int_{T_1}^{T_2} c_p dT$ , in which  $c_p$  is variable and depends on both the temperature and the pressure of the vapor. This variation is shown in Figs. 6 and 7 of the Keenan and Keyes tables. If a constant value (equal to the mean, or average, value over the temperature range) is assigned to  $c_p$ , the change of entropy may, conversely, be calculated as in Chap. 6. The result will be an approximation.

A much more detailed and complete temperature-entropy chart is included as Fig. 9 of the Keenan and Keyes tables. This chart shows not only lines of constant pressure but also lines of constant enthalpy, constant superheat, constant moisture (quality), and constant volume. The areas below the lines of constant volume, as explained in Chap. 6, are the changes of internal energy between states that they connect when that area is measured down to a temperature of absolute zero.

*Example 7:8.* Check, approximately, the tabulated values of  $s_f$  and  $s_{fg}$  at 100 psia and the tabulated value of  $s$  at 100 psia and  $400^\circ\text{F}$ .

*Solution:* Referring to Eq. (6:8),  $ds = \frac{du}{T} + \frac{P dv}{JT}$ . The change of volume of the liquid is minor, and the second term may accordingly be dropped for the purpose of our approximate calculation. At 100 psia,  $u_f$  is 298.08 Btu, and, at  $32^\circ\text{F}$ ,  $u_f$  is so slightly less than zero that it may be assumed to have that value. By definition,

$$c_v = \left( \frac{du}{dt} \right)_v \quad \text{and} \quad c_{vm} = \frac{\Delta u}{\Delta t} = \frac{298.08}{327.81 - 32} = 1.01 \text{ Btu}/(^\circ\text{F})(\text{lb})$$

Then

$$s_f = c_{vm} \int_{T_0}^T \frac{dT}{T} = 1.01 \int_{492}^{787.8} \frac{dT}{T} = 1.01 \log_e \frac{787.8}{492} = (1.01)(0.470) = 0.474$$

This checks the tabulated value in spite of the approximations introduced by dropping the second term of Eq. (6:8) and using  $c_v$  as a constant instead of a variable.



To calculate the entropy of evaporation,  $s_{fg} = \frac{h_{fg}}{T_{\text{sat}}} = \frac{888.8}{787.8} = 1.129$ . This is, in principle, an *exact* calculation. The use of the slide rule and of an approximate value for the absolute temperature of saturation account for the small discrepancy when compared with the tabulated value.

In checking the tabulated value of  $s$  at 100 psia and 400°F, it is noted that the enthalpy of superheat (the increase of enthalpy over that of the saturated vapor at the same pressure) is  $1227.6 - 1187.2 = 40.4$  Btu and that the corresponding temperature rise is  $400 - 327.81 = 72.19^\circ\text{F}$ . The mean specific heat at constant pressure is therefore

$$c_{pm} = \left( \frac{\Delta h}{\Delta t} \right)_p = \frac{40.4}{72.19} = 0.56$$

Then

$$s - s_g = c_{pm} \int_{T_{\text{sat}}}^T \frac{dT'}{T'} = 0.56 \int_{787.8}^{860} \frac{dT'}{T'} = 0.56 \log_e \frac{860}{787.8} = (0.56)(0.088) = 0.0493$$

Adding this entropy of superheat to  $s_g$ ,  $s = 0.0493 + 1.6026 = 1.6519$ . This checks the tabulated value closely, although an approximation has again been introduced in using an average value of  $c_p$  as a constant value over the entire range. As the range of temperature increased, the accuracy of this method of calculation would decrease. The tabulated values take into account this variation of specific heat and have been obtained as the result of much more careful computation than is possible in the use of the slide rule.

Lines of constant pressure corresponding to 100, 14.7, and 5 psia have not been shown for the compressed liquid in Fig. 7:5. These lines, as they move to lower temperatures, would lie so close to the saturated-liquid line that to attempt to show them on the diagram would be confusing rather than helpful. A constant-pressure line at 3206.2 psia, the critical pressure, has been shown, however, to indicate the general form of these lines in the compressed-liquid region; even for this line the divergence from the saturated-liquid line has been somewhat exaggerated. At 39°F, the temperature of greatest density of liquid water, it cuts across the saturated-liquid line and enters the liquid-vapor space of Fig. 7:5. Under this pressure the fusion temperature is lowered somewhat, as is indicated in the figure.

Lines of constant pressure lower than the critical pressure will, in the compressed-liquid space, lie between the critical-pressure isobar and the saturated-liquid line, intersecting both lines at a temperature of 39°F. Isobars for pressures above the critical pressure will fall to the left of the critical-pressure isobar but very close to it above the temperature of 39°F and will also intersect the saturated-liquid line at this temperature.

The paragraphs immediately above have indicated an overlapping of the compressed-liquid space into the liquid-vapor region on the  $T$ 's diagram. This is an unusual characteristic of water and is due to its attainment of a maximum density of the liquid at a temperature that is above the fusion temperature and to its expansion as the temperature is lowered

below 39°F. It provides an exception to the statement made earlier in these pages that, if two independent properties of the simple system, composed of a pure substance, are known, all other properties are fixed. Ice, water, and steam, or any combination of these phases, meet the specifications for a pure substance as set forth in Chap. 1. Temperature and specific entropy would constitute two independent properties. As obtained from Table 4 of the Keenan and Keyes tables, the specific entropy of compressed water at 32°F and 3206.2 psia is +0.00029, and its volume is slightly less than the volume of the saturated liquid at the same temperature. But the mixture of saturated liquid and saturated vapor at 32°F which has a quality of  $0.00029/2.1877$ , or about 0.013 per cent, would also have the same entropy and temperature and its volume would obviously be greater than that of the saturated liquid. The area of overlap is small; that fact and the almost unique character of this exception to the general rule combine to make it relatively unimportant from a practical standpoint in engineering thermodynamics, but the special characteristics of water such as that mentioned in the above lines, the lesser density of the solid phase as compared with the liquid, and the reduction of fusion temperature with increased pressure are very important in ameliorating the conditions under which life exists on the earth's surface. That water, a substance so important to the life process, should vary from the general rule certainly is significant.

**7:9. The Mollier diagram** often offers great convenience in the solution of the practical engineering problem, especially when steady-flow processes are involved (see Chap. 6). In Fig. 7:6 is shown a Mollier, or enthalpy-entropy, diagram for water; the notation corresponds with Fig. 7:5.

The saturated liquid line *amg* continues to form the saturated-vapor line *gncz*; the critical point *g* is an inflection point on this saturation line. The triple-point line extends from *b* through *a* to *c* (note that the triple point is represented by a straight line on this diagram although its coordinates are both extensive properties), *b* representing the saturated solid, *a* the saturated liquid, and *c* the saturated vapor. The space under the saturation line and above the triple-point line represents mixtures of the liquid and the vapor; that below the triple-point line is the solid-vapor area. Above the saturated-vapor line lie superheated-vapor states, and the compressed-liquid region lies just to the left of and closely borders the saturated-liquid line.

Lines representing constant pressures of 100, 14.7, and 5 psia are shown on Fig. 7:6 crossing the liquid-vapor space and extending into the superheated-vapor area above. In the liquid-vapor space these are also lines of constant temperature of, respectively, 327.8, 212, and 162.2°F. It has been shown in Chap. 6 that the slope of a constant-pressure line on the



Mollier diagram is equal to its absolute temperature, and these lines, as they cross the liquid-vapor area, are accordingly straight and diverge as they move from the saturated-liquid line to the saturated vapor line. At the point where they contact the saturated-liquid line, their pressure *and temperature* are the same as (instantaneously) for the saturated liquid, and these lines therefore leave the saturated-liquid line as tangents to that curve. As they move across the saturated-vapor line into the superheated-vapor region, the temperature, and consequently their slope, increases and they curve gradually upward in this area.

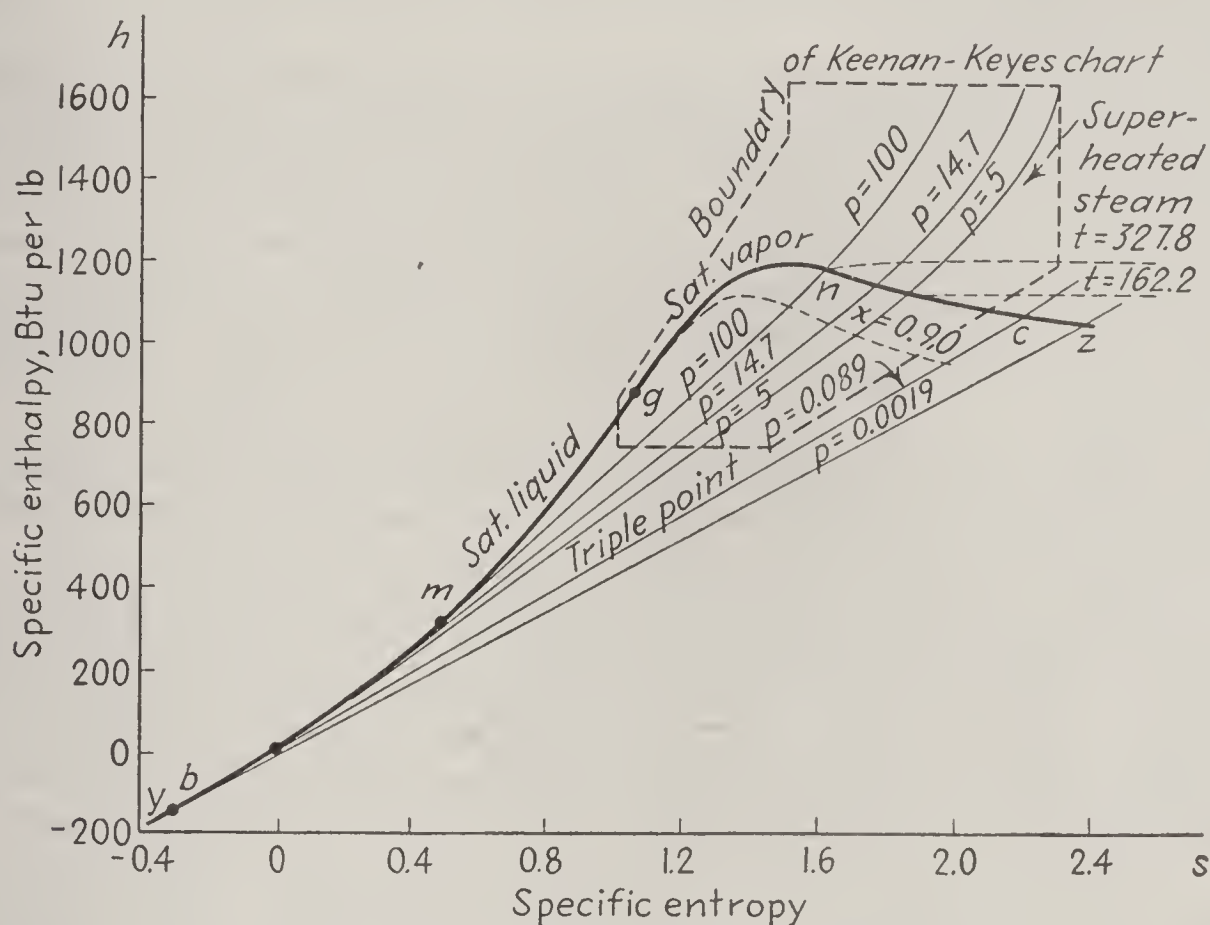


FIG. 7:6. Mollier diagram for water.

At the saturated-vapor line, the lines of constant temperature diverge from those of constant pressure and curve upward to the right. As they near the right-hand border of the figure, they become almost horizontal (constant-enthalpy) lines. Particularly is this true at the lower temperatures and pressures where the lines of constant temperature leave the saturated-vapor line as nearly horizontal lines. We shall later have occasion to recall this feature to the mind of the reader.

A reference to Eq. (7:2) will indicate that the change of enthalpy during evaporation is directly proportional to the change of quality of the mixture if the pressure is constant. Thus the intercept of a line of constant pressure between the saturated-liquid and saturated-vapor lines may be divided into, say, 10 equal parts, and the points of division between these parts may be designated as denoting states having qualities of 10, 20, and

so on, up to 90 per cent. On Fig. 7:6 the locus of the 90 per cent quality points has been connected and is a line of *constant quality*.

The practical use of the Mollier diagram is usually limited to the superheat region and the higher qualities. A large-scale Mollier chart, which covers the area indicated in Fig. 7:6, accompanies the Keenan and Keyes tables. The information it carries is, of course, much more complete and detailed than that shown in Fig. 7:6.

*Example 7:9.* Steam enters a reversible adiabatic turbine at 200 psia and 500°F and leaves at atmospheric pressure (standard). Assuming steady flow and neglecting differences in velocity and elevation between entrance and exit, what work is delivered per pound of steam flow?

*Solution.* The work per pound of flow is  $h_1 - h_2$  (see Chap. 3). The expansion that takes place in the turbine is indicated as isentropic in the statement of the problem, and thus  $s_2 = s_1$ . Referring to Table 3 of the Keenan and Keyes tables,  $h_1 = 1268.9$  Btu, and  $s_1 = 1.6240 = s_2$ . This value of 1.6240 lies between  $s_f$  and  $s_g$  at the exhaust pressure of 14.7 psia, and the exhaust from the turbine is therefore in the form of wet steam. Applying Eq. (7:2),  $s_{f_2} + xs_{fg_2} = s_1$  or  $0.3120 + 1.4446x = 1.6240$  and, solving,  $x = 0.908$ . Then  $h_2 = 1150.4 - (1 - 0.908)(970.3) = 1061.2$  Btu. The work of this ideal turbine is  $1268.9 - 1061.2 = 207.7$  Btu per pound of steam.

The use of the Mollier chart makes the solution of this problem much simpler and more rapid. Finding the intersection of a line representing a constant temperature of 500°F with the line of 200 psia pressure,  $h_1$  is read at the side of the chart as 1269 Btu. Projecting vertically downward (at constant entropy) from this point, the intersection with the line representing the exhaust pressure of 14.7 psia falls at an enthalpy ( $h_2$ ) of 1061 Btu and a moisture percentage of 9.2, equivalent to a quality of 90.8 per cent. It is observed that the accuracy in the use of the chart is at least within 1 Btu, which is sufficient for engineering uses. Even when greater accuracy is desired, the chart may be used to good effect as a check on detailed computations.

**7:10. The Experimental Determination of Quality.** The properties most readily and accurately determined by observation and experiment are the pressure and temperature. For superheated steam and compressed water these are sufficient to establish the state of the fluid; for the liquid-vapor mixture these two properties are interdependent and do not suffice to locate the proportions of the mixture. It is often necessary to determine the quality of the steam as it leaves a boiler or enters a prime mover. This can, of course, be done by making use of the greater density of the liquid to separate it from the mixture and then comparing its weight with that of the steam in which it was carried. The weight of the steam portion is usually measured by allowing it to pass through a calibrated orifice. A device of this kind is called a *separating calorimeter*.

Another method of determining the quality of wet steam is through the use of a *throttling calorimeter*. This device, illustrated in Fig. 7:7, includes a *sampling tube B*, pierced by a number of holes so located that a representative steam sample will be obtained and inserted into the steam



line, an *orifice*  $O$  through which the steam sample flows continuously into a *chamber*  $C$ , from which it flows directly into the atmosphere. Provision is also made, as shown, for determining the pressure of the steam in the line and its pressure and temperature in the calorimeter chamber. The entire calorimeter is covered by a thick layer of heat-insulating material so that the flow of steam through it may be considered adiabatic in character. The differences in velocity and elevation of the steam in the line and in the chamber may be ignored with negligible error, and no external work is performed. Applying the steady-flow energy equation of Chap. 3, it may be shown that the enthalpies in the line and in the calorimeter chamber are equal.

The use of the throttling calorimeter for the determination of quality is limited to situations where the quality of the steam in the line is high (about 95 per cent or more) and to steam-line pressures in the approximate range of 75 to 1200 psia, depending on the quality. The purpose of the throttling expansion is to change the steam sample to superheated steam so that the pressure and temperature in the calorimeter chamber will be sufficient to establish its enthalpy. This enthalpy, equal to that in the steam line, is then used in combination with line pressure to locate the quality in the line. The solution is conveniently obtained graphically by making use of the Mollier diagram. In this case, the point on the chart that represents the pressure and temperature of the superheated steam in the calorimeter chamber is located and projected horizontally (at constant enthalpy) to the left across the saturation line to the line of constant pressure corresponding to the pressure in the line. The quality in the line is read from the chart at this intersection. The throttling process does not proceed, however, at constant enthalpy; it merely begins and ends at states having equal enthalpies. As the steam passes through the orifice, there is a temporary increase of velocity at the expense of a decrease of enthalpy; as this velocity is dissipated in the chamber, the enthalpy again builds up to its upstream value.

The reason for the limitation in the use of the throttling calorimeter to the range of qualities and pressures mentioned above is made clear by

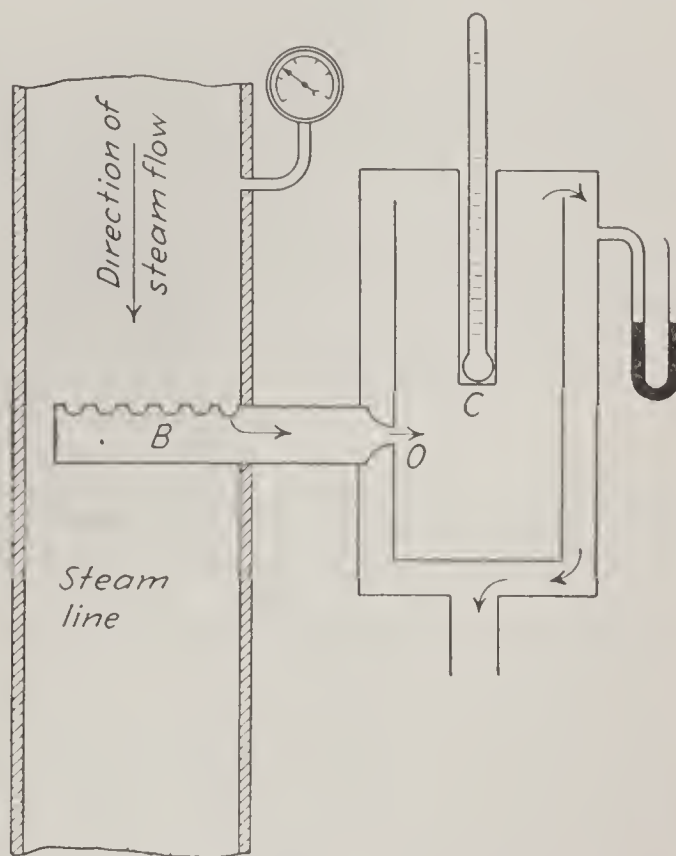


FIG. 7:7. The throttling calorimeter.

Fig. 7:8. This diagram plots the saturation temperatures of the saturated liquid and the saturated vapor as ordinates against their specific enthalpies as abscissas. A sample condition for the wet steam in the line is spotted on the diagram as the point  $L$ ; by estimating its relative distance from the saturated-liquid and saturated-steam lines, the corresponding quality of the steam in the line is seen to be about 97 per cent. The point  $C$  indicates the superheated state that is reached as the result of the

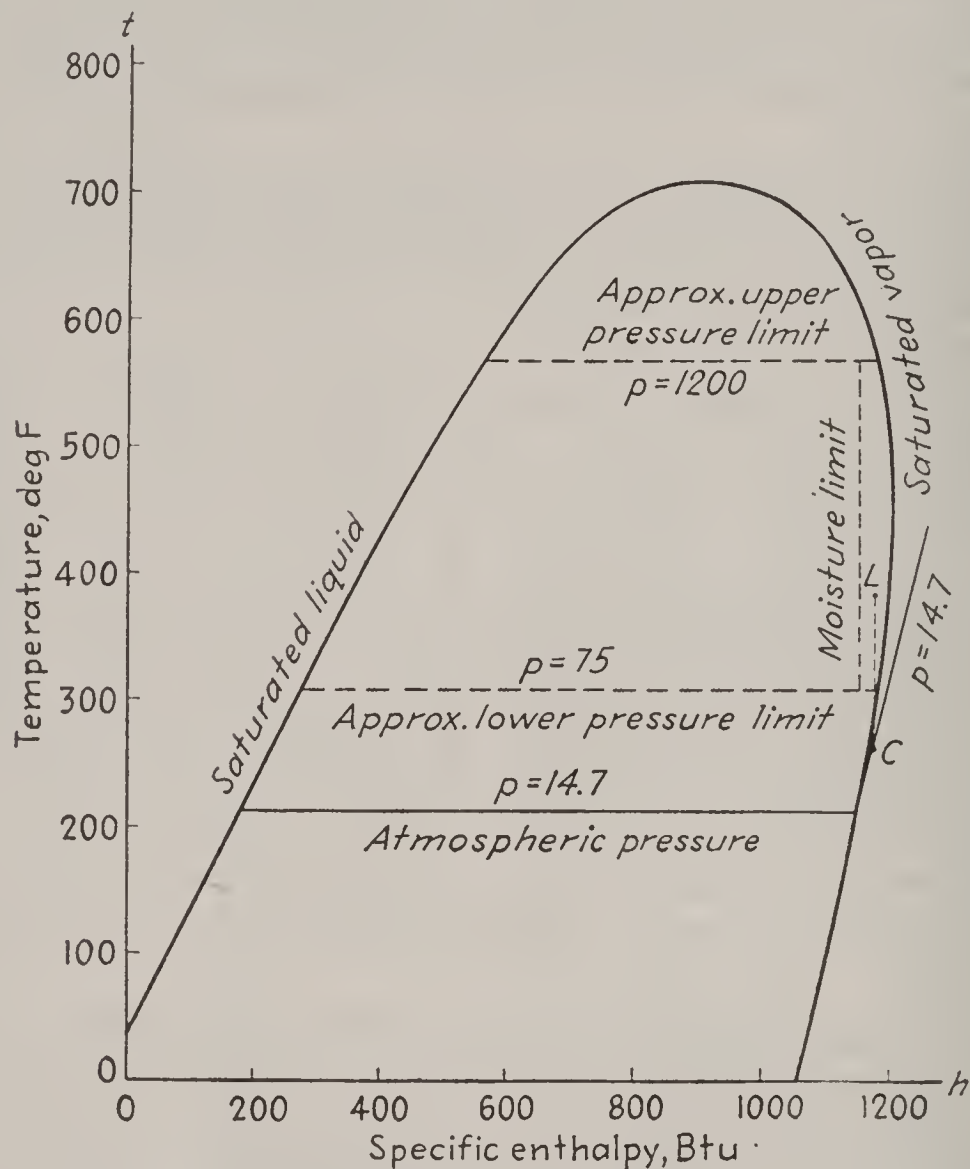


FIG. 7:8. Throttling calorimeter range.

throttling expansion. The line connecting  $L$  and  $C$  is vertical (at constant enthalpy) but is dotted to remind the reader that points along it do not correspond to intermediate states during the expansion.

The point  $C$  must lie in the superheated-steam region if the throttling calorimeter is to be usable for the determination of the quality in the line. It is apparent that if that quality is too low or line pressure too high, point  $C$  will lie either in the liquid-vapor region or so close to the saturated-steam line that the temperature at  $C$  will be very little above the saturation temperature at atmospheric pressure. A superheat of 5 to 10°F is usually considered desirable to make certain that the steam in the chamber is superheated; this also accounts for the lower limit of line pressure



which is shown on the diagram. The pressure and quality ranges can be somewhat increased by making provision for calorimeter exhaust into a space in which the pressure is less than atmospheric, as to a condenser.

*Example 7:10.* The pressure in a steam line is 200 psia. In the chamber of a throttling calorimeter, the temperature of a sampling of steam from this line has become 260°F at atmospheric pressure (standard). What is the quality of the steam in the line?

*Solution.* The state of the steam in the line will be designated by the subscript 1, that in the calorimeter as 2. Then, consulting Table 3, at  $p_2 = 14.7$  psia,  $t_2 = 260^\circ\text{F}$ ,  $h_2$  is found to be 1173.8 Btu. This is also the value of  $h_1$  and

$$h_{f_1} + x_1 h_{fg_1} = h_2 \text{ or } 355.36 + 843.0x = 1173.8$$

Solving,

$$x_1 = 0.971$$

The Mollier chart is again well adapted to the solution of the throttling-calorimeter problem. Locating the point on the chart that represents the condition in the calorimeter chamber as the intersection of the lines of 14.7 psia pressure and 260°F temperature in the superheat region above the saturation line, we need not stop to identify the enthalpy but can project horizontally (at constant enthalpy) to the left across the saturation line until the line which represents line pressure of 200 psia is intersected. At that intersection we read a moisture percentage of 2.9, corresponding to a quality of 97.1 per cent.

### Problems

1. Based on Figure 7:2, how many triple points may be observed for the pure substance  $\text{H}_2\text{O}$ ? For each, list the approximate temperature and pressure and the components of the mixture.

2. Is it possible for ice I to melt when the temperature of the ice is above 32°F? When its temperature is above 32.02°F?

3. Will a triple point appear as a point, as a line, or as an area on each of the following diagrams? (a)  $Ts$ ; (b)  $pt$ ; (c)  $hw$ ; (d)  $hs$ ; (e)  $tv$ ; (f)  $wv$ .

4. If an equilibrium mixture of water and steam is represented by point  $b$  of Fig. 7:1, what is the quality of the mixture? See Art. 7:5 for data. Show approximate location of this state on Fig. 7:4.

5. A triple-point mixture of ice, water, and steam has an enthalpy of 0 Btu and volume of 200 ft<sup>3</sup> per pound of the mixture. Determine its proportions.

6. Based on the steam tables, tabulate the values of the pressure, enthalpy, volume, entropy, and internal energy for a system consisting of 2 lb of saturated steam at the following temperatures: (a) 32°F; (b) 212°F; (c) 400°F; (d) 500°F; (e) 705.4°F.

7. The same as Prob. 6, except that the system consists of 2 lb of saturated water.

8. Tabulate the values of the temperature, enthalpy, volume, entropy, and internal energy for a system consisting of 0.5 lb of saturated steam at the following pressures: (a) 2 in. Hg abs; (b) 2 psig; (c) 14.7 psia; (d) 400 psia; (e) 500 psig; (f) 2000 psia; (g) 3206.2 psia.

9. The same as Prob. 8, except that the system consists of 0.5 lb of saturated water.

10. For steam having a quality of 98 per cent, find the pressure (or temperature), the specific volume, the specific enthalpy, the specific entropy, and the specific internal energy when (a)  $t = 32^\circ\text{F}$ ; (b)  $p = 14.7$  psia; (c)  $p = 400$  psia; (d)  $t = 400^\circ\text{F}$ .

11. An equilibrium mixture of steam and water has a specific enthalpy of 1000 Btu. Calculate its quality and its internal energy if (a)  $p = 2$  psia; (b)  $t = 212^\circ\text{F}$ ; (c)  $t = 400^\circ\text{F}$ ; (d)  $p = 3000$  psia.

12. A mixture of saturated steam and saturated water has a specific entropy of 1.25. Calculate its quality if (a)  $p = 2$  in. Hg abs; (b)  $t = 212^\circ\text{F}$ ; (c)  $p = 400$  psia; (d)  $t = 650^\circ\text{F}$ .

13. A pound of wet steam has a specific internal energy of 900 Btu. What is its quality if (a)  $p = 2$  in. Hg abs; (b)  $p = 14.7$  psia; (c)  $t = 300^\circ\text{F}$ ; (d)  $t = 500^\circ\text{F}$ ; (e)  $p = 3000$  psia?

14. Three pounds of steam is confined in a tank having an internal volume of 12 ft<sup>3</sup>. What is its quality or superheat if (a)  $p = 2$  psia; (b)  $p = 14.7$  psia; (c)  $t = 300^\circ\text{F}$ ; (d)  $t = 400^\circ\text{F}$ ; (e)  $p = 200$  psia?

15. Steam at the critical temperature and pressure is contained within a closed, rigid, and transparent tube. As the steam is cooled, its pressure and temperature decrease. Into what proportions does the meniscus divide the total internal volume of the tube as the following pressures and temperatures are reached? (a)  $p = 3000$  psia; (b)  $t = 600^\circ\text{F}$ ; (c)  $p = 700$  psia; (d)  $t = 400^\circ\text{F}$ ; (e)  $p = 67$  psia; (f)  $t = 200^\circ\text{F}$ ; (g)  $p = 2$  in. Hg abs.

16. What is the value of the psi function ( $\psi$ ) for saturated steam and for saturated water, as based on steam-table values, when  $t = 400^\circ\text{F}$ ? When  $t = 100^\circ\text{F}$ ? Write a general expression for  $\psi_{fg}$ . If the reference state at which the entropy and the enthalpy are zero were changed, would this expression still hold? For a given temperature or pressure would it give the same value for  $\psi_{fg}$ ?

17. Calculate, based on steam-table values, the value of the zeta function ( $\zeta$ ) for saturated steam and for saturated water when  $t = 400^\circ\text{F}$ ; when  $t = 100^\circ\text{F}$ . At which temperature does  $\zeta$  have the higher value? What is always the value of  $\zeta_{fg}$ ?

18. When water changes into steam at constant temperature, which is larger, the change of enthalpy or the change of internal energy? When ice I changes into water, which is the larger?

19. Tabulate the values of the volume, the enthalpy, the entropy, and the internal energy of a 1-lb superheated-steam system when the pressures and temperatures are as follows: (a) 1 psia and  $120^\circ\text{F}$ ; (b) 98.2 psia and  $400^\circ\text{F}$ ; (c) 98.2 psia and  $408^\circ\text{F}$ .

20. For the following pairs of properties, determine whether the steam is saturated or superheated and its quality or superheat. If superheated, state its pressure and temperature. (a)  $p = 100$  psia,  $h = 1200$  Btu; (b)  $p = 400$  psia,  $h = 1200$  Btu; (c)  $t = 200^\circ\text{F}$ ,  $s = 1.8000$ ; (d)  $t = 200^\circ\text{F}$ ,  $s = 1.7500$ ; (e)  $v = 3$  ft<sup>3</sup>,  $p = 100$  psia; (f)  $v = 2$  ft<sup>3</sup>,  $p = 500$  psia; (g)  $h = 1300$  Btu,  $s = 1.5000$ .

21. What is the mean specific heat at constant pressure for superheated steam at the following states? (a) 2 psia and  $200^\circ\text{F}$ ; (b) 2 psia and  $500^\circ\text{F}$ ; (c) 14.7 psia and  $500^\circ\text{F}$ ; (d) 200 psia and  $500^\circ\text{F}$ ; (e) 200 psia and  $700^\circ\text{F}$ ; (f) 500 psia and  $700^\circ\text{F}$ .

22. What is the value of  $c_{p_i}$  at the states listed in Prob. 21?

23. What is the instantaneous value of the specific heat at constant pressure for steam of quality  $x$ ?

24. For steam at  $300^\circ\text{F}$ ,  $x = 0.80$ , calculate the instantaneous value of the specific heat at constant volume. Use an interval of (a)  $4^\circ\text{F}$ ; (b)  $20^\circ\text{F}$ . If your answers do not agree, give an explanation of the reasons for the discrepancy. Which answer do you consider to be the more accurate? Why?

25. For the following paired pressures and temperatures, compute the volume, enthalpy, and entropy of 1 lb of compressed water. Use the unabridged steam tables. (a) 800 psia and  $32^\circ\text{F}$ ; (b) 4000 psia and  $32^\circ\text{F}$ ; (c) 800 psia and  $400^\circ\text{F}$ ; (d) 4000 psia and  $400^\circ\text{F}$ ; (e) 4000 psia and  $700^\circ\text{F}$ ; (f) 1900 psia and  $260^\circ\text{F}$ .



26. Work Prob. 25 on the assumption that water is incompressible, basing your calculations on data taken from Table 1 of the steam tables.

27. Saturated water at 400°F enters a pump which compresses it continuously to 2000 psia. Determine the work per pound pumped if the compression is isentropic (a) by calculation based on Table 4 of the steam tables, (b) by the use of Fig. 3 of the steam tables, and (c) from  $dh = v dP$ . What is the temperature of the water as it leaves the pump?

28. A system consists of an equilibrium mixture of 3 lb of ice, 2 lb of water, and 1 lb of steam. What are its temperature, pressure, volume, enthalpy, entropy, and internal energy?

29. A system consists of three-fourths ice, one-fourth steam at a uniform temperature of 12°F. What is its pressure? What, per pound of the mixture, are its enthalpy, volume, entropy, and internal energy?

30. Based on Fig. 7:5, show that the value of the zeta function for saturated water or steam, or superheated steam, as based on steam-table values of the properties, must always be negative. Is  $\zeta$  for the state denoted by point  $y$  (on the saturated-solid line of Fig. 7:5) positive or negative? Why?

31. Explain how Fig. 9 of the unabridged steam tables can be put to good use in speeding the solution of Prob. 20 above.

32. Steam enters a turbine at 400 psia,  $t = 600^\circ\text{F}$ , and expands adiabatically, leaving at a final pressure of 2 psia. The differences of elevation and of velocity between entrance and exit are negligible. (a) What maximum amount of shaft work may be performed per pound of steam flowing, and what is the final condition (quality or superheat) of the steam? (b) If the shaft work is 20 per cent less than the maximum, what is the final condition of the steam? Solve this problem both by calculation based on data taken from Tables 2 and 3 of the steam tables and by making use of the Mollier diagram for steam. Compare the two answers and the ease with which they were obtained.

33. The same as Prob. 32, except that the steam enters at a velocity of 100 fps and leaves at 800 fps.

34. A throttling calorimeter is used to determine the quality of the steam in a line in which the steam pressure is 300 psig. If the pressure and temperature in the expansion chamber of the calorimeter are as listed below, is it possible to fix the quality in the line? (a) 14.7 psia and 212°F; (b) 14.7 psia and 240°F; (c) 5 psia and 180°F. Where it is possible, determine the quality of the steam in the line, obtaining your answer both by calculation based on Tables 2 and 3 of the steam tables and by making use of the Mollier diagram for steam. Compare the answers and the ease with which they were obtained.

35. A closed system consisting of a pound of steam at 67 psia, quality of 0.50, expands isothermally and reversibly to a final pressure of 20 psia. What amounts of work and of heat flow accompany the process? Show the approximate state path on a  $pv$  diagram and on a  $Ts$  diagram for steam. How are the work and the heat flow shown on these diagrams?

36. The system of Prob. 35 undergoes a constant-volume reversible process as a result of which its pressure becomes 20 psia. What are its final temperature and quality (or superheat)? What amounts of work and heat flow accompany the process? Show the approximate state path on  $pv$  and  $Ts$  diagrams for steam.

37. The system of Prob. 35 expands reversibly and at constant pressure until its volume is tripled. What is its final temperature? What work and what heat flow accompany the process? Show the approximate state path on  $pv$  and  $Ts$  diagrams for steam.

38. The system of Prob. 35 is compressed reversibly and adiabatically until its pressure becomes 200 psia. Find the final temperature and quality (or superheat). What work accompanies the process? Show the approximate state path on  $pv$  and  $Ts$  diagrams for steam.

39. A Carnot engine contains 1 lb of  $H_2O$ . At the beginning of the isothermal expansion, it is a saturated liquid at 200 psia and, at the end, saturated steam ( $x = 1$ ). The adiabatic expansion is carried to a pressure of 1 psia. What is the efficiency of the cycle? What net work is performed per cycle? What is the state (quality or superheat) of the working substance at the end of the adiabatic expansion and at the beginning of the adiabatic compression? Plot this cycle on a  $Ts$  diagram for steam.

40. In steady flow around an open-system circuit, a pound of  $H_2O$  passes through the following four processes before completing the cycle: (1) Saturated water at 1 psia enters, and compressed water at 200 psia leaves, a liquid pump; the process is isentropic. (2) The water, as it leaves the pump, enters a heat exchanger and is heated reversibly at constant pressure until it becomes saturated steam. (3) Leaving the heat exchanger, the steam expands adiabatically and reversibly in an engine to a pressure of 1 psia. (4) A second heat exchanger closes the cycle as it condenses the steam reversibly and at constant pressure. What amounts of work and of heat flow accompany each of the four processes? What is the net work of the cycle? What is the efficiency of the cycle? Plot the cycle on a  $Ts$  diagram for steam. Compare the cycle and its efficiency with the results of Prob. 39.

41. A pound of ammonia (see Appendix for tables of the properties of ammonia) passes through a cycle composed of the following four open-system steady-flow processes: (1) Originally a saturated liquid at 180 psia, it is throttled adiabatically through a small opening into a space where the pressure is 30 psia. (2) It passes through a heat exchanger, receiving heat reversibly and at constant pressure until it is a saturated vapor. (3) The vapor enters a compressor and is compressed isentropically to a pressure of 180 psia. (4) The vapor leaving the compressor passes through a heat exchanger in which it is condensed reversibly and at constant pressure. What amounts of heat and work accompany each of the processes? What is the net work of the cycle? What amount of heat does the pound of ammonia *receive* in the course of the cycle? At what temperature does it receive this heat? What amount of heat does it reject? What is the lowest temperature at which heat is rejected? On a  $Ts$  diagram which shows the liquid and saturated-vapor lines for ammonia, show the appearance of this cycle. Is it a reversible cycle?

42. A pound of saturated mercury vapor at a pressure of 160 psia expands adiabatically and reversibly to a pressure of 2 psia. If the expansion takes place as a closed-system (nonflow) process, what work is performed? What is the final condition (quality or superheat) of the mercury? Answer the same questions when the process is of a steady-flow character through an open system.

### Symbols

$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$h$	enthalpy of unit mass
$J$	proportionality factor
$p$	pressure, psi
$P$	pressure, psf
$s$	entropy of unit mass
$t$	scalar temperature
$T$	absolute temperature



$u$	internal energy of unit mass
$v$	volume of unit mass
$W$	work
$x$	mass of vapor per unit mass of mixture

*Subscripts*

$f$	of the saturated liquid
$g$	of the saturated vapor
$fg$	change during vaporization
$i$	of the saturated solid; also, instantaneous value of the specific heat
$ig$	change during sublimation
$m$	mean value of the specific heat
$p$	constant pressure
sat	saturation
$v$	constant volume

## CHAPTER 8

### GENERAL THERMODYNAMIC EQUATIONS FOR THE PURE SUBSTANCE

**8:1. The Maxwell Relations.** It will be noted that the primary properties ( $p$ ,  $v$ , and  $T$ ) are of a character such that it is possible to measure their values, corresponding to a given state of the pure substance, in a direct and tangible manner. The secondary properties, such as internal energy, enthalpy, and entropy, cannot, on the other hand, be directly measured, and it becomes desirable to establish relations that will make it possible to express their values in terms of the primary properties. Assume that, as the result of experiment and research, an equation has been developed that connects the pressure, volume, and temperature of a pure substance.<sup>1</sup> It will be remembered that this equation defines a  $pvT$  surface that will include all equilibrium states within the scope of the equation. The location of any point on this surface identifies an equilibrium state of the substance and, with it, the values of all of the properties, primary or secondary.<sup>2</sup> As we move from one point on this surface to a second point, also on the surface, the change of any one property will be the same without regard to the path we may choose to follow between the two points. This is the foundation that underlies the use of Eqs. (1:4) and (1:5) in the identification of a property. Conversely, if we know  $P$ ,  $x$ , and  $y$  to be properties, we are justified in writing  $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$  [see Eq. (1:5)] as a true and correct relation between those properties.

Suppose we select the equation that represents the application of the First Law to a simple closed system of unit weight as an example. This is [see Eq. (2:5)],  $J \partial Q - \partial W = J du$ .  $\partial Q$  and  $\partial W$  are not properties but can be expressed in terms of properties if we assume a maximum-work process; the corresponding equivalents are  $T ds$  and  $P dv$ . Substituting these values and rearranging,

$$du = T ds - \frac{P dv}{J}$$

<sup>1</sup> This equation, here called the primary equation of state, will be adequate for separate phases (though a separate equation may be required for each phase) but will not normally apply to mixtures of phases since the pressure and temperature are not independent properties of such mixtures.

<sup>2</sup> The values of the secondary properties may be *relative* to some datum level, or levels, which is, as a matter of course, held constant.



Comparing, we see that this equation is in the form of Eq. (1:4) with  $M = T$  and  $N = -P/J$ . The equation is expressed entirely in terms of properties (with the exception of the constant,  $J$ ) and, following Eq. (1:5), we may write

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \quad \text{or} \quad \left( \frac{\partial T}{\partial v} \right)_s = \frac{-1}{J} \left( \frac{\partial P}{\partial s} \right)_v \quad (8:1)$$

Returning to the equation from which Eq. (8:1) was derived, we observe that, if the volume is constant,  $dv$  is zero and the second term on the right side of that equation becomes zero. Then  $(du)_v = (T ds)_v$ , or

$$\left( \frac{\partial u}{\partial s} \right)_v = T \quad (8:2)$$

Similarly, when the entropy is constant,  $ds = 0$ , and

$$\left( \frac{\partial u}{\partial v} \right)_s = \frac{-P}{J} \quad (8:3)$$

(For an illustration of this relation, see Fig. 2:8.) Proceeding in a similar manner,

$$h = u + \frac{Pv}{J} \quad dh = du + \frac{P dv}{J} + \frac{v dP}{J}$$

But

$$T ds = du + \frac{P dv}{J}$$

and, substituting,

$$dh = T ds + \frac{v dP}{J}$$

from which we obtain

$$\left( \frac{\partial T}{\partial P} \right)_s = \frac{1}{J} \left( \frac{\partial v}{\partial s} \right)_P \quad (8:4)$$

and, holding  $s$  and  $P$  constant, successively,

$$\left( \frac{\partial h}{\partial P} \right)_s = \frac{v}{J} \quad (8:5)$$

and

$$\left( \frac{\partial h}{\partial s} \right)_P = T \quad (8:6)$$

Applying the same methods to the psi property,

$$\psi = u - Ts$$

$$d\psi = du - T ds - s dT = du - \left( du + \frac{P dv}{J} \right) - s dT = -\frac{P dv}{J} - s dT$$

and

$$\frac{1}{J} \left( \frac{\partial P}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T \quad (8:7)$$

$$\left( \frac{\partial \psi}{\partial T} \right)_v = -s \quad (8:8)$$

$$\left( \frac{\partial \psi}{\partial v} \right)_T = -\frac{P}{J} \quad (8:9)$$

From the definition of the zeta property as

$$\zeta = u + \frac{Pv}{J} - Ts$$

$$\begin{aligned} d\zeta &= du + \frac{P}{J} dv + \frac{v}{J} dP - T ds - s dT = \left( du + \frac{P}{J} dv - T ds \right) \\ &\quad + \frac{v}{J} dP - s dT \\ &= 0 + \frac{v}{J} dP - s dT \end{aligned}$$

and

$$\frac{1}{J} \left( \frac{\partial v}{\partial T} \right)_P = - \left( \frac{\partial s}{\partial P} \right)_T \quad (8:10)$$

$$\left( \frac{\partial \zeta}{\partial T} \right)_P = -s \quad (8:11)$$

$$\left( \frac{\partial \zeta}{\partial P} \right)_T = \frac{v}{J} \quad (8:12)$$

Equations (8:1) to (8:12) are known as the *Maxwell relations*. They furnish a basis from which many other equations of similar nature may be developed. For example, comparing Eqs. (8:2) and (8:6), we see that

$$\left( \frac{\partial u}{\partial s} \right)_v = \left( \frac{\partial h}{\partial s} \right)_P \quad (8:13)$$

and, making other similar comparisons,

$$\left( \frac{\partial u}{\partial v} \right)_s = \left( \frac{\partial \psi}{\partial v} \right)_T \quad (8:14)$$

$$\left( \frac{\partial h}{\partial P} \right)_s = \left( \frac{\partial \zeta}{\partial P} \right)_T \quad (8:15)$$

$$\left( \frac{\partial \psi}{\partial T} \right)_v = \left( \frac{\partial \zeta}{\partial T} \right)_P \quad (8:16)$$

*Example 8:1.* Check, approximately, Maxwell relations (8:1) to (8:12) for superheated steam at 90 psia and 380°F.

*Solution.* Table 3 of the Keenan and Keyes tables will be used. It will be noted that it will be desirable to extend the tabulation to cover the values of the internal



energy, the psi, and the zeta properties. At the designated state the calculation of these properties is as follows:

$$u = h - \frac{Pv}{J} = 1218.6 - \frac{(144)(90)(5.359)}{778} = 1218.6 - 89.3 = 1129.3 \text{ Btu}$$
$$\psi = u - Ts = 1129.3 - (840)(1.6523) = 1129.3 - 1388.0 = -258.7 \text{ Btu}$$
$$\zeta = h - Ts = 1218.6 - 1388.0 = -169.4 \text{ Btu}$$

To speed our calculation it will be convenient to extend the tabulation to include surrounding states. The result is shown below:

<i>p</i>		370°F	380°F	390°F
89 psia	<i>v</i>	5.346	5.422	5.497
	<i>h</i>	1213.4	1218.7	1224.0
	<i>s</i>	1.6473	1.6537	1.6600
	<i>u</i>	1125.4	1129.4	1133.4
	$\psi$	-241.9	-259.7	-277.6
	$\zeta$	-153.9	-170.4	-187.0
90 psia	<i>v</i>	5.284	5.359	5.434
	<i>h</i>	1213.2	1218.6	1223.9
	<i>s</i>	1.6459	1.6523	1.6586
	<i>u</i>	1125.2	1129.3	1133.3
	$\psi$	-240.9	-258.7	-276.5
	$\zeta$	-152.9	-169.4	-185.9
91 psia	<i>v</i>	5.223	5.298	5.372
	<i>h</i>	1213.0	1218.4	1223.7
	<i>s</i>	1.6445	1.6509	1.6572
	<i>u</i>	1125.1	1129.2	1133.2
	$\psi$	-239.8	-257.6	-275.4
	$\zeta$	-151.9	-168.4	-184.9

(a) Checking Eq. (8:1)

$$\left(\frac{\partial T}{\partial v}\right)_s = -\frac{1}{J}\left(\frac{\partial P}{\partial s}\right)_v$$

Here *s* and *v* are successively held constant. The value of *s* at the designated state is 1.6523. At 89 psia, this value falls between 370 and 380°F, interpolation showing the temperature to be approximately 377.8°F with a corresponding volume of 5.405 ft³. At 91 psia, interpolation shows the temperature and volume corresponding to this entropy to be, respectively, 382.2°F and 5.314 ft³. Then

$$\left(\frac{\partial T}{\partial v}\right)_s = \frac{382.2 - 377.8}{5.314 - 5.405} = \frac{4.4}{-0.091} = -48.3$$

Similarly, the value of *v* at the designated state is 5.359 ft³, and this corresponds, at 89 psia, to a temperature of 371.7°F and entropy of 1.6484 and, at 91 psia, to a temperature of 388.3°F and entropy of 1.6561. Then

$$-\frac{1}{J}\left(\frac{\partial P}{\partial s}\right)_v = \frac{-144(91 - 89)}{778(1.6561 - 1.6484)} = -48.0$$

Comparing with the value of  $\left(\frac{\partial T}{\partial v}\right)_s$  above, the relatively small discrepancy may be attributed to the small number of significant places in the differences that enter into these calculations.

(b) Eq. (8:2):  $\left(\frac{\partial u}{\partial s}\right)_v = T$ . Here  $v$  is again constant as in the second half of part *a*.

At 89 psia, 371.7°F (see part *a*), the internal energy is 1126.1 Btu, and, at 91 psia, 388.3°F,  $u = 1132.5$  Btu. The corresponding entropies may be taken from part *a*.

Then

$$\left(\frac{\partial u}{\partial s}\right)_v = \frac{1132.5 - 1126.1}{1.6561 - 1.6484} = 831; T = 380 + 460 = 840$$

(c) Eq. (8:3):  $\left(\frac{\partial u}{\partial v}\right)_s = -\frac{P}{J}$ . Here  $s$  is constant. At 89 psia, 377.8°F, and at 91 psia, 382.2°F (see part *a*), the internal energies are, respectively, 1128.5 and 1130.0 Btu. The corresponding volumes may be taken from part *a*. Then

$$\left(\frac{\partial u}{\partial v}\right)_s = \frac{1130.0 - 1128.5}{5.314 - 5.405} = -16.5; -\frac{P}{J} = \frac{(-144)(90)}{778} = -16.7$$

(d) Eq. (8:4):  $\left(\frac{\partial T}{\partial P}\right)_s = \frac{1}{J} \left(\frac{\partial v}{\partial s}\right)_P$ . From part *a*,

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{382.2 - 377.8}{144(91 - 89)} = 0.0153$$

Directly from the table above,

$$\frac{1}{J} \left(\frac{\partial v}{\partial s}\right)_P = \left(\frac{1}{778}\right) \left(\frac{5.434 - 5.284}{1.6586 - 1.6459}\right) = 0.0152$$

(e) Eq. (8:5):  $\left(\frac{\partial h}{\partial P}\right)_s = \frac{v}{J}$ . At 89 psia, 377.8°F, the enthalpy is 1217.5 Btu, and, at 91 psia, 382.2°F,  $h = 1219.6$  Btu. Then

$$\left(\frac{\partial h}{\partial P}\right)_s = \frac{1219.6 - 1217.5}{144(91 - 89)} = 0.0073; \frac{v}{J} = \frac{5.359}{778} = 0.0069$$

(f) Eq. (8:6):  $\left(\frac{\partial h}{\partial s}\right)_P = T$ . Directly from the table,

$$\left(\frac{\partial h}{\partial s}\right)_P = \frac{1223.9 - 1213.2}{1.6586 - 1.6459} = 842; T = 840$$

(g) Eq. (8:7):  $\frac{1}{J} \left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$ . From data computed in part *a*,

$$\frac{1}{J} \left(\frac{\partial P}{\partial T}\right)_v = \frac{144(91 - 89)}{778(388.3 - 371.7)} = 0.0223$$

Directly from the table,

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1.6509 - 1.6537}{5.298 - 5.422} = 0.0226$$

(h) Eq. (8:8):  $\left(\frac{\partial \psi}{\partial T}\right)_v = -s$ . At 89 psia, 371.7°F,  $\psi$  is -244.9 Btu, and, at 91 psia, 388.3°F,  $\psi = -272.4$  Btu. Then

$$\left(\frac{\partial \psi}{\partial T}\right)_v = \frac{-272.4 - (-244.9)}{388.3 - 371.7} = -1.66; -s = -1.6523$$



(i) Eq. (8:9):  $\left(\frac{\partial\psi}{\partial v}\right)_T = -\frac{P}{J}$ . Directly from the table,

$$\left(\frac{\partial\psi}{\partial v}\right)_T = \frac{-257.6 - (-259.7)}{5.298 - 5.422} = -16.9; -\frac{P}{J} = -16.7$$

(j) Eq. (8:10):  $\frac{1}{J}\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T$ . All data may be taken directly from the table.

$$\begin{aligned} \frac{1}{J}\left(\frac{\partial v}{\partial T}\right)_P &= \left(\frac{1}{778}\right)\left(\frac{5.434 - 5.284}{390 - 370}\right) = 0.0000096; \\ &\quad -\left(\frac{\partial s}{\partial P}\right)_T = -\frac{1.6509 - 1.6537}{144(91 - 89)} = 0.0000097 \end{aligned}$$

(k) Eq. (8:11):  $\left(\frac{\partial\zeta}{\partial T}\right)_P = -s$ . Substituting values read directly from the table,

$$\left(\frac{\partial\zeta}{\partial T}\right)_P = \frac{-185.9 - (-152.9)}{390 - 370} = -1.65; -s = -1.6523$$

(l) Eq. (8:12):  $\left(\frac{\partial\zeta}{\partial P}\right)_T = \frac{v}{J}$ . Again directly from the table,

$$\left(\frac{\partial\zeta}{\partial P}\right)_T = \frac{-168.4 - (-170.4)}{144(91 - 89)} = 0.0069; \frac{v}{J} = 0.0069$$

**8:2. The specific heats** at constant volume and constant pressure are themselves derivatives of properties. The specific heat at constant volume has been defined (see Chap. 2) as  $c_v = \left(\frac{\partial u}{\partial T}\right)_v$ . Based on Eq. (8:2),

$$\left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

or

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v \quad (8:17)$$

Similarly, employing Eq. (8:6),

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P \quad (8:18)$$

Equations (8:17) and (8:18) express the specific heats in terms of the entropy. The change of the specific heats with respect to changes in the primary properties may also be derived. From Eqs. (8:17) and (8:7),

$$c_v = T \left(\frac{\partial s}{\partial T}\right)_v \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{J} \left(\frac{\partial P}{\partial T}\right)_v$$

Then,

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \frac{\partial}{\partial v} \left(\frac{\partial s}{\partial T}\right)_v = T \frac{\partial}{\partial T} \left(\frac{\partial s}{\partial v}\right)_T = \frac{T}{J} \frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T}\right)_v = \frac{T}{J} \left(\frac{\partial^2 P}{\partial T^2}\right)_v \quad (8:19)$$

Proceeding in a similar manner, but making use of Eqs. (8:18) and (8:10), it may be shown that

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -\frac{T}{J} \left(\frac{\partial^2 v}{\partial T^2}\right)_P \quad (8:20)$$

By means of Eqs. (8:19) and (8:20) and a primary equation of state, a limited number of specific heat data may be extended to cover a wider range of states.

We learn from the calculus that the relation between the partial derivatives of any three point functions<sup>1</sup> is

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (8:21)$$

This equation may be used to good effect to establish certain interesting and useful relations between properties. For example, the ratio of the specific heat at constant pressure to the specific heat at constant volume,  $c_p/c_v$  (usually called simply the *ratio of the specific heats* and designated by the symbol  $k$ ), may be expressed in terms of derivatives of the properties with its aid. If we select the primary properties as the point functions, Eq. (8:21) becomes

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1 \quad (8:22)$$

From Eq. (8:17),

$$c_v = T \left(\frac{\partial s}{\partial T}\right)_v \quad \text{or} \quad \frac{c_v}{T} \left(\frac{\partial T}{\partial s}\right)_v = 1$$

Then

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{c_v}{T} \left(\frac{\partial T}{\partial s}\right)_v \left(\frac{\partial P}{\partial T}\right)_v = \frac{c_v}{T} \left(\frac{\partial P}{\partial s}\right)_v$$

But, from Eq. (8:1),

$$\left(\frac{\partial P}{\partial s}\right)_v = -J \left(\frac{\partial T}{\partial v}\right)_s$$

and, substituting above,

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{Jc_v}{T} \left(\frac{\partial T}{\partial v}\right)_s \quad (8:23)$$

Similarly,

$$c_p = T \left(\frac{\partial s}{\partial T}\right)_P \quad \text{or} \quad \frac{T}{c_p} \left(\frac{\partial s}{\partial T}\right)_P = 1$$

$$\left(\frac{\partial T}{\partial v}\right)_P = \frac{T}{c_p} \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial T}{\partial v}\right)_P = \frac{T}{c_p} \left(\frac{\partial s}{\partial v}\right)_P$$

<sup>1</sup> A point function is a coordinate of a point. When three point functions are involved, the point lies on a surface such as the  $pvT$  surface. Properties are therefore point functions, and, for the pure substance, three are necessary to establish the location of the points.



and, making the substitution suggested by Eq. (8:4),

$$\left(\frac{\partial T}{\partial v}\right)_P = \frac{T}{Jc_p} \left(\frac{\partial P}{\partial T}\right)_s \quad (8:24)$$

Making the substitutions in Eq. (8:22) that are suggested by Eqs. (8:23) and (8:24), we have

$$- \frac{Jc_v}{T} \left(\frac{\partial T}{\partial v}\right)_s \frac{T}{Jc_p} \left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial v}{\partial P}\right)_T = -1$$

and, solving for  $c_p/c_v$ , we obtain

$$k = \frac{c_p}{c_v} = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial v}{\partial P}\right)_T = \left(\frac{\partial P}{\partial v}\right)_s \left(\frac{\partial v}{\partial P}\right)_T \quad (8:25)$$

*Example 8:2A.* Estimate, for superheated steam at 90 psia, 380°F, the specific heats at constant volume and at constant pressure and the ratio of the specific heats, using Eqs. (8:17), (8:18), and (8:25). Compare with the corresponding values as obtained directly from the definitions of these properties.

*Solution:*

(a) Eq. (8:17):  $c_v = T \left(\frac{\partial s}{\partial T}\right)_v$ . Using data from Example 8:1, the volume is the same at 89 psia, 371.7°F, and at 91 psia, 388.3°F, as at the designated state. At the first of these two states the entropy is 1.6484 and, at the second, 1.6561. Then

$$c_v = 840 \left( \frac{1.6561 - 1.6484}{388.3 - 371.7} \right) = 0.39$$

But  $c_v = \left(\frac{\partial u}{\partial T}\right)_v$  by definition, or, again using values from Example 8:1,

$$c_v = \frac{1132.5 - 1126.1}{388.3 - 371.7} = 0.386$$

(b) Eq. (8:18):  $c_p = T \left(\frac{\partial s}{\partial T}\right)_P$ , or, using the table of Example 8:1,

$$c_p = 840 \left( \frac{1.6586 - 1.6459}{390 - 370} \right) = 0.532$$

By definition,

$$c_p = \left(\frac{\partial h}{\partial T}\right)_P = \frac{1223.9 - 1213.2}{390 - 370} = 0.535$$

(c) Eq. (8:19):  $k = \left(\frac{\partial P}{\partial v}\right)_s \left(\frac{\partial v}{\partial P}\right)_T$ . Again using the data of Example 8:1,

$$k = \left[ \frac{144(91 - 89)}{5.314 - 5.405} \right] \left[ \frac{5.298 - 5.422}{144(91 - 89)} \right] = 1.36$$

Based on the values of  $c_p$  and  $c_v$  as computed from Eqs. (8:18) and (8:17),

$$k = \frac{c_p}{c_v} = \frac{0.532}{0.39} = 1.36$$

Based on the definitions of  $c_p$  and  $c_v$ ,

$$k = \frac{0.535}{0.386} = 1.38$$

*Example 8:2B.* Show that, for a gas having a primary equation of state in the form of Eq. (1:6), the internal energy, the enthalpy, the specific heat at constant volume, the specific heat at constant pressure are all functions of the temperature alone, *i.e.*, are independent of changes in the pressure or the volume.

*Solution:*

(a) For the reversible process,  $du = T ds - \frac{P dv}{J}$ . Dividing through by  $dv$  and writing the equation as it applies to a reversible isothermal,

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - \frac{P}{J}$$

But, from Eq. 8:7,

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{J} \left(\frac{\partial P}{\partial T}\right)_v$$

and, substituting,

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{T}{J} \left(\frac{\partial P}{\partial T}\right)_v - \frac{P}{J}$$

The equation of state is  $pv = CT$  or  $P = 144CT/v$ , and

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{T}{J} \left(\frac{\partial P}{\partial T}\right)_v - \frac{P}{J} = \frac{T}{J} \frac{144C}{v} - \frac{P}{J} = \frac{P}{J} - \frac{P}{J} = 0$$

The internal energy of this gas is therefore independent of volume changes if  $T$  is constant. Also,  $\left(\frac{\partial u}{\partial P}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = 0 \times \left(\frac{\partial v}{\partial P}\right)_T = 0$ , and  $u$  is also independent of pressure changes at constant  $T$ .<sup>1</sup>

(b) It has been shown in part *a* that  $u$  is a function of temperature alone. But  $h = u + Pv/J$ , and  $Pv/J (= 144pv/J)$  is also a function of the temperature alone, the product  $pv$  having a constant value for this gas if the temperature does not change. Therefore the enthalpy is independent of pressure and volume changes except as a change in the *product*  $pv$  indicates that a change in temperature has taken place.

(c) From Eq. (8:19),

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{T}{J} \left(\frac{\partial^2 P}{\partial T^2}\right)_v = \frac{T}{J} (0) = 0$$

and

$$\left(\frac{\partial c_v}{\partial P}\right)_T = \left(\frac{\partial c_v}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = 0$$

(d) Similar reasoning, based on Eq. (8:20), will show that  $c_p$  is, for this gas, independent of pressure and volume.

<sup>1</sup> As the pressure approaches zero,  $\left(\frac{\partial v}{\partial P}\right)_T$  approaches infinity. At zero pressure,  $\left(\frac{\partial u}{\partial P}\right)_T$  therefore is not necessarily zero.



Another example of the application of Eq. (8:21) to thermodynamic purposes is found when it is written in the form

$$\left(\frac{\partial T}{\partial h}\right)_P \left(\frac{\partial P}{\partial T}\right)_h \left(\frac{\partial h}{\partial P}\right)_T = -1 \quad (8:26)$$

$\left(\frac{\partial T}{\partial h}\right)_P$  is the reciprocal of the specific heat at constant pressure, or  $1/c_p$ .

The second partial derivative is the reciprocal of a ratio which is readily obtained experimentally and which is known as the *Joule-Thomson coefficient*; the symbol used to represent this coefficient is  $\mu_J$ . The experimental method employed is to allow the slow flow of a fluid through a horizontal tube which is fitted with a porous plug. The pressure and temperature upstream from the plug are held constant as the downstream pressure is gradually reduced. Provision is made for measuring pressure and temperature both upstream and downstream. As the downstream pressure is gradually reduced, the temperature below the plug that corresponds to each downstream pressure is noted and plotted as the ordinate with the pressure as the abscissa. The points so obtained are connected to form a curve. Application of the steady-flow energy equation [Eq. (3:5)], with the difference between upstream and downstream velocities assumed to be negligible, shows that for this adiabatic process (the tube is insulated to prevent appreciable heat flow) the upstream and downstream enthalpies are equal. The slope of the curve may therefore be expressed as  $\left(\frac{\partial T}{\partial P}\right)_h$  and gives the value of  $\mu_J$ , the Joule-Thomson coefficient. The Joule-Thomson coefficient is usually positive (the change of temperature across the plug usually being negative), but exceptions are found.

The Joule-Thomson apparatus may be adapted to the experimental determination of another property derivative by including a heating (or cooling) element in the porous plug. By adjusting the rate of heat flow, the downstream temperature is held at the upstream value so that the process now takes place at constant temperature. The flow is no longer adiabatic, and Eq. (3:5) indicates that the heat flow per pound of fluid flow is numerically equal to the change of specific enthalpy across the plug. If this heat flow is measured by some suitable means and plotted as the ordinate with the pressure as the abscissa, the slope of the resulting curve is  $\left(\frac{\partial h}{\partial P}\right)_T$ . This slope is called the *constant-temperature coefficient*; we shall denote it by the letter  $c$ . For the same substance at the same state,  $c$  will always have a sign opposite to that of  $\mu_J$ .

Substituting the equivalent symbols in Eq. (8:26),

$$\frac{1}{c_p} \frac{1}{\mu_J} c = -1 \quad \text{or} \quad c_p = -\frac{c}{\mu_J} \quad (8:27)$$

This equation may be used as a check on the values of  $c_p$  as obtained by other means.

*Example 8:2C.* From steam-table values, estimate the Joule-Thomson and the constant-temperature coefficients for steam at 90 psia, 380°F. Compute the specific heat at constant pressure based on Eq. (8:27), and compare with the values as obtained in Example 8:2A.

*Solution:*

(a) At 90 psia, 380°F,  $h = 1218.6$  Btu. At 80 psia, this enthalpy corresponds to a temperature of 376.8°F and, at 100 psia, to 383.3°F. The Joule-Thomson coefficient may be calculated from these values as

$$\mu_J = \left( \frac{\partial T}{\partial P} \right)_h = \frac{376.8 - 383.3}{80 - 100} = 0.325^\circ\text{F/psi}$$

(b) A similar calculation of the constant-temperature coefficient, based on the same pressure range, is

$$c = \left( \frac{\partial h}{\partial P} \right)_T = \frac{1220.3 - 1216.8}{80 - 100} = -0.175 \text{ Btu/psi}$$

(c) From Eq. (8:27),

$$c_p = -\frac{c}{\mu_J} = -\frac{(-0.175)}{0.325} = 0.538$$

The comparative values from Example 8:2A are 0.532 and 0.535.

**8:3. The General Equations for Enthalpy, Internal Energy, and Entropy.** We have applied the adjective primary to the properties that can alone be directly and tangibly measured and to the equation of state that connects those properties. This equation of state is customarily expressed either in the form  $v = f(p, T)$  or as  $p = f(v, T)$ . If the primary equation of state is as simple as Eq. (1:6), either of these two forms may, of course, readily be converted to the other but that is not generally the case. As an example, consider the primary equation of state for steam that is presented on page 15 of the Keenan and Keyes tables, and contemplate the difficulty of changing it to the form  $p = f(v, T)$ .

We now face the problem of developing secondary equations of state to apply to the intangible properties of enthalpy, internal energy, entropy, etc., expressing these properties in terms of the primary properties and their derivatives. The Maxwell relations furnish a set of tools to aid in the accomplishment of this purpose. The particular tool or tools which we select for the purpose will depend upon which form of the primary equation of state is available to us and also upon the character of additional information (such as experimentally determined values of the specific heat at constant pressure or of the Joule-Thomson coefficient) that is at hand.

For example, we may set up a general equation of state expressing the enthalpy as shown below. It is a principle of the calculus that  $dy =$



$\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$  when three variables are involved. Then

$$\begin{aligned} dh &= du + \frac{P}{J} dv + \frac{v}{J} dP = T ds + \frac{v}{J} dP \\ &= T \left(\frac{\partial s}{\partial T}\right)_P dT + T \left(\frac{\partial s}{\partial P}\right)_T dP + \frac{v}{J} dP \\ &= c_p dT - \left[ -T \left(\frac{\partial s}{\partial P}\right)_T - \frac{v}{J} \right] dP \end{aligned}$$

Substituting  $\frac{1}{J} \left(\frac{\partial v}{\partial T}\right)_P$  for  $-\left(\frac{\partial s}{\partial P}\right)_T$  [see Eq. (8:10)],

$$dh = c_p dT - \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] \frac{dP}{J} \quad (8:28)$$

and, integrating,

$$h = \int_{T_1}^T c_p dT - \frac{1}{J} \int_{P_1}^P \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] dP + h_1 \quad (8:29)$$

in which  $h_1$  is a constant of integration, being the enthalpy at some reference level at which the pressure is  $P_1$  and the temperature  $T_1$ . A study of the procedure used in the development above will indicate that the total change of enthalpy has resulted from two steps, the first term of Eq. (8:29) giving the change of enthalpy that takes place as the pressure is held constant while the temperature changes to its final value and the second term the increment of enthalpy as the temperature remains constant while the pressure is adjusted to its final value. For the purpose of the integration indicated in the second term of that equation,  $T$  is therefore handled as a constant. This equation would apply most conveniently when the primary equation of state was in the form  $v = f(p, T)$ .

*Example 8:3A.* Develop an expression for the change of enthalpy of a gas with a primary equation of state in the form  $pv = CT$ .

*Solution:*

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT - \frac{1}{J} \int_{P_1}^{P_2} \left[ T \left(\frac{\partial v}{\partial T}\right)_P - v \right] dP$$

For this gas,  $v = \frac{CT}{p}$  and  $T \left(\frac{\partial v}{\partial T}\right)_P - v = T \left(\frac{C}{p}\right) - v = v - v = 0$ . The integration between pressure limits therefore vanishes and

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT$$

or if  $c_p$  is constant,

$$h_2 - h_1 = c_p(T_2 - T_1)$$

The general equation for internal energy may be obtained in a similar manner:

$$\begin{aligned} du &= T ds - \frac{P dv}{J} = T \left( \frac{\partial s}{\partial T} \right)_v dT + T \left( \frac{\partial s}{\partial v} \right)_T dv - \frac{P dv}{J} \\ &= c_v dT + \left[ T \left( \frac{\partial s}{\partial v} \right)_T - \frac{P}{J} \right] dv \end{aligned}$$

Substituting  $\frac{1}{J} \left( \frac{\partial P}{\partial T} \right)_v$  for  $\left( \frac{\partial s}{\partial v} \right)_T$  [see Eq. (8:7)],

$$du = c_v dT + \frac{1}{J} \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv \quad (8:30)$$

and, integrating,

$$u = \int_{T_1}^T c_v dT + \frac{1}{J} \int_{v_1}^v \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] dv + u_1 \quad (8:31)$$

*Example 8:3B.* A primary equation of state is in the form  $P = \frac{RT}{v-b} - \frac{a}{v^2}$ , where  $R$ ,  $a$ , and  $b$  are constants.<sup>1</sup> Write an expression for the change of internal energy of a substance that obeys this  $pvT$  relation.

*Solution:*

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{v-b} \text{ and } T \left( \frac{\partial P}{\partial T} \right)_v - P = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2}$$

Then, from Eq. (8:30),

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT + \frac{1}{J} \int_{v_1}^{v_2} \frac{a}{v^2} dv = \int_{T_1}^{T_2} c_v dT - \frac{a}{J} \left( \frac{1}{v_2} - \frac{1}{v_1} \right)$$

Proceeding to the development of a general equation for entropy, we observe that, from Eq. (6:8),  $ds = \frac{du}{T} + \frac{P dv}{JT}$ . Substituting the value of  $du$  as expressed in Eq. (8:30),

$$\begin{aligned} ds &= \frac{du}{T} + \frac{P dv}{JT} = \frac{c_v dT}{T} + \frac{1}{J} \left[ \left( \frac{\partial P}{\partial T} \right)_v - \frac{P}{T} \right] dv + \frac{P dv}{JT} \\ &= c_v \frac{dT}{T} + \frac{1}{J} \left( \frac{\partial P}{\partial T} \right)_v dv \end{aligned} \quad (8:32)$$

Integrating,

$$s = \int_{T_1}^T c_v \frac{dT}{T} + \frac{1}{J} \int_{v_1}^v \left( \frac{\partial P}{\partial T} \right)_v dv + s_1 \quad (8:33)$$

Equations (8:30) to (8:33) are examples of forms of the general equation most conveniently used when the primary equation of state is in the form  $p = f(v, T)$ . Note that the general method of development has

<sup>1</sup> This is the van der Waals equation. It represents an attempt to fit a single form of primary equation of state to a wide range of pure substances, the constants being based on the temperature, pressure, and volume at the critical state of the substance. The equation will be discussed in greater detail in a later chapter.



differed from that followed in developing Eqs. (8:28) and (8:29) only in the use of a constant-volume step, instead of a constant-pressure, for the measurement of the first increment of the property.

If we start with  $dh = T ds + v dP/J$  (see Art. 8:1), alternate expressions for  $ds$  and  $s$  may be obtained in which the increments of entropy are measured over constant-pressure and constant-temperature segments. These are

$$ds = c_p \frac{dT}{T} - \frac{1}{J} \left( \frac{\partial v}{\partial T} \right)_P dP \quad (8:34)$$

and

$$s = \int_{T_1}^T c_p \frac{dT}{T} - \frac{1}{J} \int_{P_1}^P \left( \frac{\partial v}{\partial T} \right)_P dP + s_1 \quad (8:35)$$

**Example 8:3C.** Develop an expression for the change of entropy that is based on the van der Waals equation (see Example 8:3B).

**Solution.** The van der Waals equation is in the form  $p = f(v, T)$ . Equation (8:32) will therefore be preferable to Eq. (8:34) in the solution of this example.

$$s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} + \frac{1}{J} \int_{v_1}^{v_2} \left( \frac{\partial P}{\partial T} \right)_v dv = \int_{T_1}^{T_2} c_v \frac{dT}{T} + \frac{1}{J} \int_{v_1}^{v_2} \frac{R dv}{v - b}$$

and if  $c_v$  is constant, this becomes

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + \frac{R}{J} \log_e \frac{v_2 - b}{v_1 - b}$$

**8:4. The Clapeyron relation** is based on the Maxwell relation that is stated as Eq. (8:7) and applies this relation to mixtures of phases for which the pressure and temperature are not independent properties, *i.e.*, the pressure is a function of the temperature alone without regard to a variation of the other properties. This makes it possible to substitute  $\frac{dP}{dT}$  for  $\left( \frac{\partial P}{\partial T} \right)_v$  in Eq. (8:7) for such mixtures, and the Maxwell relation becomes

$$J \left( \frac{\partial s}{\partial v} \right)_T = \frac{dP}{dT}$$

When a change takes place at constant temperature (and, of course, constant pressure),

$$\left( \frac{\partial s}{\partial v} \right)_T = \frac{s_2 - s_1}{v_2 - v_1} = \frac{1}{J} \frac{dP}{dT} \quad (8:36)$$

where the subscripts refer, respectively, to the saturated states of the two phases. Thus, if the change is from a saturated liquid to a saturated vapor,  $s_2 - s_1 = s_g - s_f = s_{fg}$  and  $v_2 - v_1 = v_g - v_f = v_{fg}$ . Substituting in Eq. (8:36),

$$\frac{s_{fg}}{v_{fg}} = \frac{1}{J} \frac{dP}{dT}$$

The application of Eq. (8:36) is not limited to changes between the saturated-liquid and saturated-vapor states but may be applied to any change of phase, partial or complete, of the pure substance that takes place at constant temperature.

From Eq. (8:6),  $\left(\frac{\partial h}{\partial s}\right)_P = T$ . For a two-phase mixture,  $T$  will be constant if  $P$  is constant, and we may write  $\left(\frac{\partial h}{\partial s}\right)_T = T$ . Then

$$\left(\frac{\partial h}{\partial v}\right)_T = \left(\frac{\partial h}{\partial s}\right)_T \left(\frac{\partial s}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T = \frac{T}{J} \frac{dP}{dT}$$

Making the equivalent change in Eq. (8:36), we may write

$$\frac{h_2 - h_1}{v_2 - v_1} = \frac{T}{J} \frac{dP}{dT} \quad (8:37)$$

It is Eq. (8:37) that is known as the *Clapeyron relation*. Its possible uses in connection with two-phase mixtures are obvious.

**Example 8:4.** Check the steam-table values of (a) the enthalpy of vaporization at 90 psia and (b) the enthalpy of sublimation at 20°F, using steam-table data for the pressure-temperature relation and the change of volume that accompanies the change in phase and applying the Clapeyron relation.

*Solution:*

(a)  $dP/dT$  will be calculated as  $\Delta P/\Delta T$  over the range 88 to 92 psia, or

$$\frac{dP}{dT} \cong \frac{144(92 - 88)}{321.83 - 318.68} = 183 \quad [\text{Table 1, Keenan and Keyes tables}]$$

$$h_2 - h_1 = h_{fg} = \frac{T}{J} \frac{dP}{dT} (v_g - v_f) = \left(\frac{780.27}{778}\right) (183)(4.896 - 0.018) = 895 \text{ Btu}$$

The steam-table value is 894.7 Btu.

(b)  $\Delta P/\Delta T$  will be calculated over the range 15 to 25°F in Table 5 of the Keenan and Keyes tables.

$$\frac{dP}{dT} \cong \frac{144(0.0640 - 0.0396)}{25 - 15} = 0.351$$

$$h_2 - h_1 = h_{ig} = \frac{T}{J} \frac{dP}{dT} (v_g - v_i) = \left(\frac{480}{778}\right) (0.351)(5658 - 0.02) = 1225 \text{ Btu}$$

The steam-table value is 1219.9 Btu.

### Problems

1. Check, approximately, Maxwell relations (8:1) to (8:12) for superheated steam at 200 psia and 600°F.
2. Using the data of Table 3 of the steam tables, estimate the specific heats at constant volume and at constant pressure and the ratio  $k$  for superheated steam at 200 psia, as based on Eqs. (8:17), (8:18), and (8:25).
3. Show in detail the proof that  $c_p$  for an ideal gas is a function of temperature alone if it varies at all (see Example 8:2B, part d).
4. Based on the Maxwell relations, prove that lines of constant pressure on a Mollier diagram (a) are straight lines as they cross the saturated region for any vapor



and (b) are concave upward in the superheat region. (c) Prove that the critical point must be a point of inflection on the saturated liquid-saturated vapor curve as plotted on a Mollier diagram.

5. What are the coordinates of each of the following charts? (a) Lines of constant entropy have a slope proportional to the volume of the system. (b) Lines of constant volume have a slope proportional to the absolute temperature of the system. (c) Lines of constant pressure have a slope proportional to the absolute temperature of the system. (d) Lines of constant temperature have a slope proportional to the volume of the system.

6. What Maxwell relation shows that the increase of kinetic energy of the fluid per unit decrease of its pressure in adiabatic and reversible steady flow through a horizontal nozzle is proportional to its specific volume?

7. Prove that  $c_p - c_v = \frac{T}{J} \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial v}{\partial T} \right)_P$  by following the procedure outlined below:

(a) Write the expression for  $ds$  as the sum of the partial derivatives of  $s$  with respect to  $T$  and  $v$ .

(b) Write the expression for  $dv$  as the sum of the partial derivatives of  $v$  with respect to  $T$  and  $P$ .

(c) Substitute  $dv$  from (b) in (a).

(d) Write the expression for  $ds$  as the sum of the partial derivatives of  $s$  with respect to  $T$  and  $P$ .

(e) Equate the coefficients of  $dT$  in (c) and (d), and multiply both sides of the equality by  $T$ . Substitute  $c_p$  for  $T(\partial s/\partial T)_P$  [see Eq. (8:18)] and  $c_v$  for  $T(\partial s/\partial T)_v$  [see Eq. (8:17)] in this equation.

(f) Make the substitution in (e) which is suggested by Eq. (8:7), and rearrange to the required form.

8. Using the expression for the difference between the specific heats which was developed in Prob. 7, show that this difference is, for a gas having a primary equation of state in the form of Eq. (1:6), equal to  $144C/J$ .

9. Calculate from steam-table data the values of the Joule-Thomson coefficient and the constant-temperature coefficient for steam at 200 psia and 600°F. Show that the values obtained are consistent with the specific heat at constant pressure as calculated in Prob. 2.

10. In Eq. (8:21), substitute the internal energy, the volume, and the absolute temperature as the point functions, and obtain a relation analogous to Eq. (8:27). Show that one of the components of this relation is  $c_v$ , and explain how the values of the others might be established experimentally. Are these experiments performed on an open or a closed system? Is the Joule-Thomson coefficient obtained by experiment on an open or a closed system?

11. Would you classify the Joule-Thomson coefficient as a property of the system? Could it be used as a coordinate in plotting the state of the system?

12. In a Joule-Thomson experiment, the upstream pressure and temperature of a gas are 20 psia and 35°F, respectively. The downstream pressure is 15 psia, and the downstream temperature is 35.6°F. It is also observed that if the temperature is to be the same at the two points, 0.41 Btu of heat must be removed per pound of gas flow between the two sections. What is the Joule-Thomson coefficient? The constant-temperature coefficient? The specific heat at constant pressure?

13. Show that the Joule-Thomson coefficient and the constant-temperature coefficient of an ideal gas must both be zero. When these values are substituted in Eq. (8:27), what value is obtained for  $c_p$ ?

14. Develop expressions for the change of enthalpy, of internal energy, and of

entropy for a substance for which the primary equation of state may be expressed as  $P(v - b) = CT$ , in which  $b$  and  $C$  are constants.

15. Develop expressions for the changes of internal energy and of entropy of an ideal gas.

16. Check the relative values of  $s_{fg}$ ,  $v_{fg}$ , and  $h_{fg}$  as shown in the steam tables for saturated steam at 200 psia, using the Clapeyron relation.

17. At 50°F the saturation pressure of a vapor is 89.19 psia, and the change in specific volume during vaporization is 3.27 ft<sup>3</sup>. At 52°F the saturation pressure is 92.66 psia and, at 48°F, 85.82 psia. What are the changes of enthalpy and of entropy during vaporization at 50°F?

18. For a certain substance, the change of specific volume during vaporization at 70°F and 49.62 psia is 1.574 ft<sup>3</sup>, and 148.9 Btu of heat is required to accomplish the vaporization of 1 lb reversibly. Estimate the saturation pressure at a temperature of 72°F.

19. Prove that if the melting temperature of a substance increases with the pressure applied on its surface, the specific volume of the resulting liquid is larger than that of the solid with which it is in temperature-pressure equilibrium.

20. Note that in Fig. 7:2 the boundary line that separates ice I from ice III is nearly horizontal. What does this indicate with regard to the change of enthalpy which accompanies the change from ice I to ice III? Also note that, at the triple point at which a mixture of ice I, ice III, and liquid water is possible, the slope of the fusion locus changes from negative to positive. What conclusions can you draw as to the change of volume as ice I changes to ice III?

### Symbols

$a, b$	constants
$c$	constant-temperature coefficient
$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$h$	enthalpy of unit mass
$J$	proportionality factor
$k$	ratio of the specific heats, $c_p/c_v$
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	heat flow
$R$	a constant
$s$	entropy of unit mass
$T$	absolute temperature
$u$	internal energy of unit mass
$v$	volume of unit mass
$W$	work

### Greek Letters

$\zeta$	zeta property of unit mass
$\mu_J$	Joule-Thomson coefficient
$\psi$	psi property of unit mass

### Subscripts

$h$	constant enthalpy
$p$	constant pressure
$s$	constant entropy
$T$	constant temperature
$v$	constant volume



## CHAPTER 9

### THE PERFECT GAS

**9:1. The Gas and the Vapor.** In preceding pages the terms gas and vapor have been used interchangeably. Let us now adopt a distinction between these terms. Many of the substances dealt with by the engineer remain in the gas phase during the series of processes through which he puts them. An example is the air that enters the cylinder of an internal-combustion engine or an air compressor; at no time during the cycle carried out in the apparatus does the air condense to liquid form or, indeed, even closely approach that phase. On the other hand, some substances change back and forth between separate phases in the course of the engineering cycle; the water that is the working fluid in the steam power plant furnishes an example. To distinguish between the two terms as we shall hereafter apply them, *gas* will be used when, in the course of the proposed process or processes, the substance will remain in the form of a gas; the use of *vapor* will indicate that a change in phase is contemplated. Thus the same substance may be classified as a gas for one set of operations, as a vapor for a second series of processes. When, in the course of the contemplated operations, the temperature remains above the critical temperature and the pressure never rises above the critical pressure, the classification as a gas would unquestionably be justified according to the convention we have adopted. Even if the temperature falls below the critical temperature but remains above the saturation temperature equivalent to the coexisting pressure, according to the pressure-temperature relation for the substance, the designation as a gas would apply. It will be observed that the classification as gas or vapor is closely connected with the pressure and temperature at the critical point as compared with the lowest temperature and highest pressure to be experienced during the proposed state changes.

Many substances, including, for example, hydrogen, oxygen, and nitrogen, were formerly called *permanent* gases because no usual series of engineering operations would bring about their liquefaction; yet all of these so-called "permanent" gases may be changed to the liquid phase if sufficiently large decreases of temperature and (possibly) increases of pressure are applied.

Many of the cycles soon to be discussed are gas cycles, *i.e.*, at no point in the cycle does the substance become a liquid. As gases, all substances

behave in a somewhat similar manner; this is particularly true at pressures that are low relative to their critical pressure. In order to avoid diverting attention from more essential features in the coming study of the gas cycle, it will be convenient to assume a hypothetical substance having a simple equation of state, one which can be easily handled mathematically. Yet this equation of state should relate the pressure, volume, and temperature in a manner such as to reflect, as accurately as is practicable, the actual relations between these properties for the real gases with which the engineer works. That, briefly, is the reasoning behind the concept of the ideal, or *perfect*, gas.

**9:2. The Perfect Gas.** The work of Robert Boyle with air systems at moderate temperature resulted in the statement that has come to be known as *Boyle's law*: *As a gas system is compressed or expanded at a constant temperature, the product of its pressure and volume will remain constant.* In mathematical terms, Boyle's law may be stated as

$$(PV)_T = C \quad \text{or} \quad \frac{P_1}{P_2} = \frac{v_2}{v_1} \quad (T \text{ const}) \quad (9:1)$$

Boyle's investigations were made in the seventeenth century. The later work of Charles and others lead to the modern version of *Charles' law*:

1. *If the pressure is constant during the expansion or compression of a gas system, the volume will vary directly with the absolute temperature.*

2. *If the volume is constant, the absolute pressure will vary directly with the absolute temperature.*

Or, stated mathematically,

1. At constant pressure,

$$\frac{v_1}{v_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{v}{T} = C \quad (9:2)$$

2. At constant volume,

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{P}{T} = C \quad (9:3)$$

More recent investigation has shown that the laws of neither Boyle nor Charles are exact over a wide range of states. However, at pressures that are low relative to the critical pressure and temperatures which are high relative to the critical temperature, both reflect quite accurately the behavior of the gas. Indeed, as they apply to hydrogen or helium, these laws supply a method for the determination of temperatures on the thermodynamic scale. As the temperature is lowered, the product  $PV$  in the Boyle's law equation (9:1) will approach zero as a limit. The absolute zero of temperature corresponding to this limit must be found



by extrapolation, of course, since absolute zero of temperature cannot be attained, nor would any substance remain a gas at that temperature. The instrument employed is called a constant-volume or a constant-pressure thermometer according to whether the volume or the pressure of the gas system is held constant as the temperature is changed between arbitrarily defined anchor points of temperature.

Air is an important gas from the engineering standpoint. The error incurred in applying the Boyle and Charles relations to air at atmospheric pressure is about one-tenth of 1 per cent and, at 300 psia, approximately 1 per cent. For more exact computations, corrections are necessary, especially at high pressures, but, for the immediate purpose of developing approximate equations to apply to real gases, the accuracy of these laws is sufficient to justify their use in framing a primary equation of state for the so-called perfect gas. Moreover, Eqs. (9:1) to (9:3) present very simple relations between the primary properties, leading to an uncomplicated primary equation of state.

The restrictions on the use of the Boyle and Charles relations, if they are to give accurate results, to states in the low-pressure or high-temperature range lead to the concept of the perfect gas as having an extremely large volume for a given number of molecules, so large, in fact, that the attractive forces between molecules vanish and energy storage in the molecular system is solely due to molecular mass and velocity (the kinetic energy of the molecule). Moreover, because they are so widely separated, collisions between molecules would not occur.

The rate of storage of energy in the system composed of what we call a perfect gas may be calculated mathematically on the basis of the kinetic theory of matter if the velocity of the molecule is assumed to be entirely translational in character. This would be the case for a molecule composed of only a single atom; this molecule could be said to have three degrees of freedom of motion, the  $X$ ,  $Y$ , and  $Z$  directions of Fig. 9:1.<sup>1</sup>

<sup>1</sup> Molecules composed of more than a single atom could have rotational and vibrational kinetic energy as well as translational. For instance, a diatomic (two-atom) molecule could have not only the three degrees of freedom of translational motion but could also rotate about either of two axes perpendicular to each other and to a line joining the two atoms. This would be classified as two additional degrees of freedom of motion, or a total of five for the diatomic molecule when rotational energy is taken into account. (Rotation about the axis that joins the two atoms is possible but represents a negligible amount of energy.) For molecules containing more than two atoms, the number of degrees of freedom of motion is still greater. Kinetic energy of vibration is the result of a motion of the atoms of a molecule relative to each other, thus changing the pattern of the molecule in rapid periodic fashion. This type of motion does not make its appearance in important degree except at the higher temperatures but may account for an additional two degrees of freedom of motion of the diatomic molecule.

Let us consider a unit volume of a perfect gas confined within the cubical container represented by the dashed lines of the figure; the edges of the cube are, of course, of unit length.

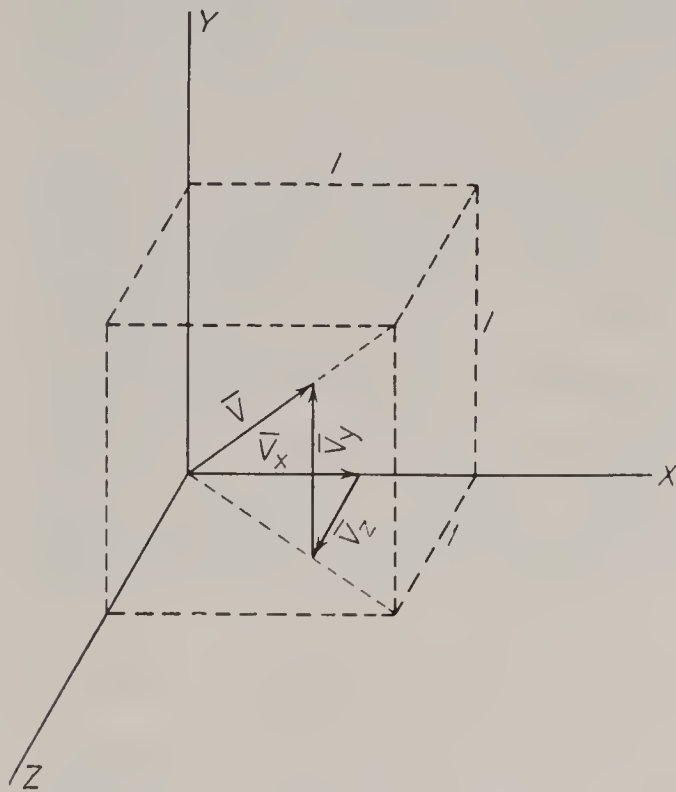


FIG. 9:1. Translational molecular motion.

It will be assumed, to conform to the kinetic theory of matter, that the number of individual molecules in the container is very large, and we shall designate that number as  $N$ . We shall further assume, for the present, that only a single perfect gas is contained and that the mass  $m$  is therefore the same for each molecule. Further, it will be assumed that the gas system is in temperature and pressure equilibrium so that the absolute velocity of every molecule is the same (although they move in different directions at a given instant). The immense number of molecules and the helter-skelter nature of their movement make it possible to represent their

average direction as along the diagonal of the cube as indicated by the vector  $\bar{V}$  of Fig. 9:1. The components of this average velocity in the  $X$ ,  $Y$ , and  $Z$  directions will be designated as  $\bar{V}_x$ ,  $\bar{V}_y$ , and  $\bar{V}_z$ , respectively. These components are equal and, since  $\bar{V}^2 = \bar{V}_x^2 + \bar{V}_y^2 + \bar{V}_z^2$ , may be expressed as  $\bar{V}/\sqrt{3}$ .

The pressure exerted against the walls of the container is the effect produced by the bombardment of those walls by the perfectly elastic molecules. We may calculate the intensity of this pressure if we study the impulse exerted by a single molecule, moving in the average direction of all of the molecules of the system, against the walls of the container, multiplying this single effect by the total of the number of molecules in the system. When this average molecule strikes the right vertical wall of the cubical container and rebounds, the component of velocity  $\bar{V}_x$  is reversed and the change in velocity that occurs is  $2\bar{V}_x$ ; neither of the components  $\bar{V}_y$  or  $\bar{V}_z$  is affected since the reaction force applied by the wall on the molecule, which causes the molecule to rebound, can be only in a direction normal to the wall. The impulse applied on the wall by this collision is equal to the change of momentum of the molecule, or  $2m\bar{V}_x$ . This molecule will return to the left vertical wall and, rebounding from that wall, will again strike the right wall in the time  $2/\bar{V}_x$ , since the perpendicular distance between the walls is unity and the (unreduced) velocity in the direction of that perpendicular is  $\bar{V}_x$ . The number of



collisions per second is therefore  $\bar{V}_x/2$ , and the force exerted against the right wall is, accordingly,

$$f_x = 2m\bar{V}_x \frac{\bar{V}_x}{2} = m\bar{V}_x^2$$

or, for  $N$  molecules and since the side of the cube is of unit area,

$$F_x = Nm\bar{V}_x^2 = P_x = \frac{Nm\bar{V}^2}{3}$$

To justify our selection of the diagonal of the cube as representing the average direction of molecular movement, note that  $P_y$  and  $P_z$  are equal to  $P_x$  when this selection is made and that this is a condition necessary to the stable equilibrium of the system.  $P_x$  may therefore be replaced by  $P$ , the pressure of the gas system.

The total mass of the molecules of the system is  $Nm$ , and this is the mass of a system of unit volume so that  $Nm = \rho$ , the mass density of the perfect-gas system. Thus the pressure exerted by the system is

$$P = \frac{1}{3}\rho\bar{V}^2$$

We may substitute  $1/v$  for  $\rho$  for this simple system, and thus

$$Pv = \frac{1}{3}\bar{V}^2 \quad (9:4)$$

This relation will later prove to be important in the calculation of the specific heats of the perfect gas (Art 9:4).

When two or more gases comprise a mixture, the effects of the bombardments of the walls by each type of molecule may be separated and the result called the *partial pressures* of the constituents. The gases will differ in the masses and the velocities of their molecules. Then

$$P_a = \frac{1}{3}N_a m_a \bar{V}_a^2 \quad P_b = \frac{1}{3}N_b m_b \bar{V}_b^2 \quad \text{etc.} \quad (9:5)$$

The total pressure of the mixture is the sum of these partial pressures, or

$$P_m = P_a + P_b + \cdots + P_n \quad (9:6)$$

*Dalton's law* states this relation as follows: *The total pressure of a mixture of perfect gases is the sum of the partial pressures that would be exerted by the constituent gases at mixture temperature and mixture volume.*

When Eqs. (9:1) to (9:3) are combined to allow a variation of all three of the primary properties, the primary equation of state of the perfect gas results as

$$Pv = RT \quad (9:7)$$

in which  $R$  is a constant, called the *gas constant*. The gas constant is not dimensionless; analysis will show that it has the dimensions of length/

temperature. If Eq. (9:7) is differentiated with  $P$  constant,

$$P dv = R dT \quad (9:8)$$

$P dv$  is the work that accompanies a reversible process (in this case, a reversible constant-pressure process). Analyzing Eq. (9:8), we see that  $R$  is the work that is performed during the reversible constant-pressure expansion of unit weight of the perfect gas while the temperature increases by 1 deg. On this basis, the dimensions of  $R$  are work per pound per degree Fahrenheit.

Equation (9:7) has been written for unit weight of the gas. For a perfect-gas system of weight  $M$ , both sides of that equation may be multiplied by the weight, or

$$MPv = PV = MRT \quad (9:9)$$

The *molecular weight*  $m$  of a substance gives a value to the relative weight of its molecule. For instance,  $m$  for oxygen is 32 and, for carbon dioxide, 44. The *mole* is defined as an amount of a substance that has a weight equal to its molecular weight; the mole of oxygen, as we shall use it, will have a weight of 32 pounds (called the pound-mole) although other units of weight, such as the gram (the gram-mole, abbreviated g-mole), are also used. One mole thus contains the same standard number of molecules for any gas (or, indeed, any liquid or solid).

If the substance is a perfect gas, Eq. (9:9) may be applied to a weight equal, in pounds, to its molecular weight  $m$ , giving

$$PV_m = mRT \quad (9:10)$$

in which  $V_m$  is the molar volume, or volume of 1 mole. Observing that, in Eq. (9:7),  $R$  is proportional to the specific volume at given pressure and temperature, the product  $mR$  in Eq. (9:10) is seen to have the same value for any perfect gas. This product, called the *universal gas constant*, has a value of, approximately, 1545 ft-lb/(°R)(mole). For the gram-mole, the corresponding value of the universal gas constant may be shown to be 0.848 kg-m/(°K)(g-mole). Note that we shall use no prefix to designate the pound-mole.

When the universal gas constant is substituted for  $mR$  in Eq. (9:10), the molar volume  $V_m$  is observed to have the same value for any perfect gas when the pressure and temperature are the same. This leads directly to Avogadro's law: *At identical temperature and pressure, equal volumes of all gases contain the same number of molecules.* This statement, originally framed to apply to *all* gases, is exact for perfect gases. Since  $mR = 1545$  ft-lb/(°R)(mole), we may calculate the gas constant  $R$  for any gas as the quotient obtained by dividing the universal gas constant



by the molecular weight of that gas, or

$$R = \frac{1545}{m}$$

(9:11)

Applied to oxygen, this gives a value of  $R$  for that gas of  $\frac{1545}{32} = 48.3$ . Equation (9:11) is often particularly useful when the gas system consists of a mixture of individual gases. In this case, if the proportions of the mixture are known, the weighted average molecular weight (called the *apparent molecular weight*) may be calculated and a value of  $R$  obtained from Eq. (9:11) to apply to the mixture. Thereafter Eqs. (9:7) and (9:9) may be applied to the mixture exactly as if the system had been a single gas. Air is, of course, such a mixture; the value of  $R$  for air is 53.3.

TABLE 9:1. APPROXIMATE DATA FOR GASES

Name	Formula	Mol. wt $m$	Gas constant $R$	$c_p^*$ Btu/(lb)(°F)	$c_v^*$ Btu/(lb)(°F)	$k^*$
Air.....	.....	28.97	53.3	0.240	0.171	1.40
Carbon dioxide.....	CO <sub>2</sub>	44	35.1	0.201	0.156	1.29
Carbon monoxide...	CO	28	55.2	0.248	0.177	1.40
Helium.....	He	4.002	386.0	1.25	0.755	1.66
Hydrogen.....	H <sub>2</sub>	2.016	766.6	3.42	2.43	1.41
Nitrogen.....	N <sub>2</sub>	28.016	55.2	0.248	0.177	1.40
Oxygen.....	O <sub>2</sub>	32	48.3	0.217	0.155	1.40
Water.....	H <sub>2</sub> O	18.016	85.8	0.45	0.34	1.32

\* Approximate values at atmospheric temperature.

Table 9:1 tabulates approximate data for certain gases of general interest to the engineer. The value of the gas constant has been obtained by the use of Eq. (9:11). The specific heats are approximate and are those which apply at atmospheric levels of temperature.

*Example 9:2A.* Derive Eq. (9:7) from the laws of Boyle and Charles.

*Solution.* Let the initial pressure, specific volume, and temperature be represented by  $P_1$ ,  $v_1$ , and  $T_1$  and the final values of these properties at the end of a certain change of state by  $P_2$ ,  $v_2$ , and  $T_2$ . The change will be accomplished in two steps, during the first of which the pressure is constant at  $P_1$  as the temperature changes to its final value  $T_2$ ; during the second step, the temperature will be constant at  $T_2$  as the pressure attains its final value  $P_2$ . The specific volume at the end of the first step will be denoted as  $v'$ . For the first step, applying Eq. (9:2),

$$\frac{v_1}{v'} = \frac{T_1}{T_2} \text{ or } v' = \frac{v_1 T_2}{T_1}$$

and, for the second step, making use of Eq. (9:1),

$$P_1 v' = P_2 v_2 \text{ or } v' = \frac{P_2 v_2}{P_1}$$

Equating the two values of  $v'$ ,

$$\frac{v_1 T_2}{T_1} = \frac{P_2 v_2}{P_1} \quad \text{or} \quad \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

from which  $Pv/T = \text{a constant} = R$ , or  $Pv = RT$ .

*Example 9:2B.* Based on the assumption that it is a perfect gas, calculate (a) the density of methane ( $\text{CH}_4$ ) at a pressure of 30 psia and temperature of  $100^\circ\text{F}$  and (b) the molar volume at the same pressure and temperature.

*Solution.* The molecular weight of methane is  $12 + (4)(1.008) = 16.032$ .

$$(a) \quad R = \frac{1545}{16.032} = 96.4$$

$$w = \frac{1}{v} = \frac{P}{RT} = \frac{(30)(144)}{(96.4)(560)} = 0.08 \text{ lb/ft}^3$$

$$(b) \quad V_m = \frac{1545T}{P} = \frac{(1545)(560)}{(30)(144)} = 200 \text{ ft}^3$$

*Example 9:2C.* Show that  $R$  will always be the maximum work that can accompany the constant-pressure expansion of a perfect-gas system of unit weight as the temperature increases by 1 deg, without regard for the initial pressure or temperature that is assumed.

*Solution.* The maximum work is  $P(v_2 - v_1)$ .

$$v_1 = \frac{RT_1}{P_1}; v_2 = \frac{RT_2}{P_2} = \frac{R(T_1 + 1)}{P_1}; v_2 - v_1 = v_1 \left( \frac{T_1 + 1}{T_1} - 1 \right) = v_1 \frac{1}{T_1}$$

$$P(v_2 - v_1) = P_1 v_1 \frac{1}{T_1} = \frac{P_1 v_1}{T_1} = R$$

**9:3. Joule's law** states: *The internal energy of a gas is independent of the volume and depends only on the temperature of the gas.* Joule arrived at this conclusion as the result of a famous series of experiments. Two vessels were connected by a pipe and valve and immersed in a bath of water. One of the vessels contained air at high pressure; the other was evacuated. When the valve was opened and the pressure was equalized between the vessels, Joule observed no change in air or water temperature. No external work had been performed, and the constant temperature of the water bath indicated that there had been no heat flow; he therefore concluded that there had been no change of internal energy and stated his law accordingly. Later investigation, based on more critical measurements and more refined apparatus, showed that all real gases deviate at least slightly from the behavior which Joule observed; the deviation for gases which, like air and hydrogen, are not easily liquefied, is very small. This deviation is expressed in terms of the Joule coefficient which is defined as  $\mu = \left( \frac{\partial T}{\partial P} \right)_u$ ; its similarity to the Joule-Thomson coefficient,  $\mu_J$ , will be noted. The first applies to a non-flow process, the second to a process involving continuous flow.

It may be shown that Joule's law will hold exactly for the perfect gas.



The perfect gas is defined by the primary equation of state,  $Pv = RT$ . This equation conforms to Eq. (1:6) when  $R$  has the value  $144C$ , and Eq. (1:6) is therefore one form of the primary equation of state of the perfect gas. It was shown in Chap. 8 (Example 8:2B) that the internal energy of this gas (now recognized as a perfect gas) is a function of the temperature alone and is independent of the volume. The general definition of the specific heat at constant volume as  $c_v = \left(\frac{\partial u}{\partial T}\right)_v$  may therefore be changed, *as it applies to a perfect gas*, to the form

$$c_v = \frac{du}{dT} \quad (\text{perfect gas}) \quad (9:12)$$

Moreover, it was additionally proved in Example 8:2B that the enthalpy of the perfect gas is also, like the internal energy, a function of the temperature alone. The general definition of  $c_p$  as  $\left(\frac{\partial h}{\partial T}\right)_p$  therefore becomes, *for the perfect gas*,

$$c_p = \frac{dh}{dT} \quad (9:13)$$

Reference to Eq. (9:7) indicates that a line of constant temperature as drawn on a  $PV$  chart for any perfect-gas system would correspond to a locus for which the product of pressure and volume is constant and would therefore appear as a hyperbola. But it has been shown that all points along this line of constant temperature also represent states of equal internal energy and equal enthalpy. This is illustrated in Fig.

9:2; the lines of respectively constant temperature  $T_1$  and  $T_2$  are also labeled  $U_1$  and  $U_2$  and  $H_1$  and  $H_2$ , to indicate that these properties are also the same for all points along them. The line  $ab$  represents a constant volume process connecting points on the two lines; the change of internal energy that accompanies this process is

$$U_b - U_a = U_2 - U_1 = M \int_{T_1}^{T_2} c_v dT \quad (9:14)$$

Turning now to the process represented by  $cd$ , a constant-pressure process, we observe that the change of internal energy ( $U_d - U_c = U_2 - U_1$ ) is the same as for constant-volume process  $ab$  and therefore is measured by

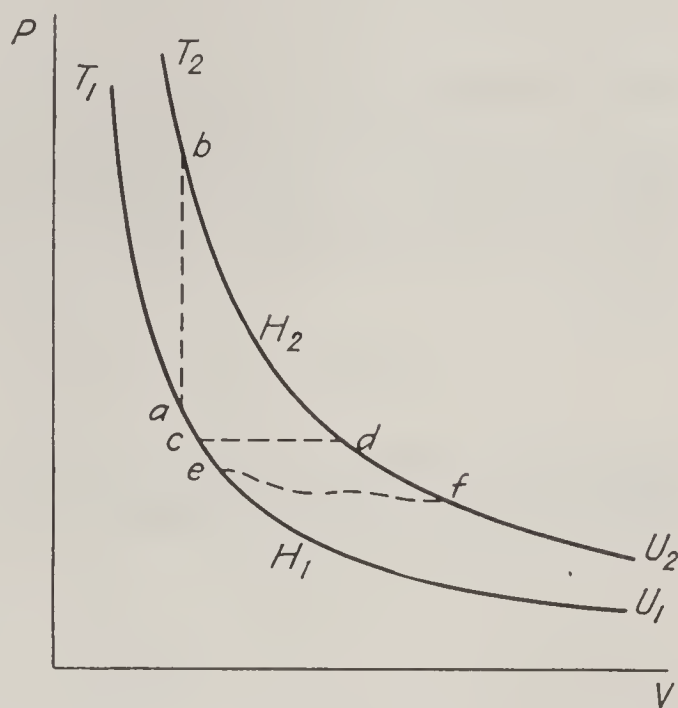


FIG. 9:2. Internal energy and enthalpy changes for a perfect gas.

applying Eq. (9:14). This could be the case only if  $c_v$  is either constant or a function of the temperature alone. This has been shown to be the case in Example 8:2B. Continuing, we may show by a similar reasoning procedure that, for any process that begins at temperature  $T_1$  and ends at temperature  $T_2$  (such as process  $ef$  of the figure), Eq. (9:14) will furnish a means of evaluating the change of internal energy.

Similarly, it may be shown that the change of enthalpy for constant-pressure process  $cd$  is

$$H_d - H_c = H_2 - H_1 = M \int_{T_1}^{T_2} c_p dT \quad (9:15)$$

and that this expression will also measure the change of enthalpy of the system over any process (such as  $ab$  or  $ef$ ) that begins at temperature  $T_1$  and ends at temperature  $T_2$ .

It has been shown above [see Eq. (9:8) *et seq.*] that  $R$  measures the work performed as a closed system of unit weight expands reversibly at constant pressure owing to a unit increase of temperature, or  $R = \frac{(\partial W)_{P, \text{rev}}}{dT}$ .

The accompanying change of internal energy,  $du$ , is, from Eq. (9:14), equal to  $c_v dT$  for a perfect-gas system, and the heat flow,  $(\partial Q)_{P, \text{rev}}$ , is, differentiating Eq. (2:9), equal to  $dh$  and therefore to  $c_p dT$ . Substituting these values in Eq. (2:5), we obtain

$$c_p dT - \frac{R}{J} dT = c_v dT \quad \text{or} \quad c_p - c_v = \frac{R}{J} \quad (9:16)$$

From this relation and the ratio of the specific heats ( $k = c_p/c_v$ ), other useful relations may be obtained, as follows:

$$c_p = \frac{kR}{J(k - 1)} \quad (9:17)$$

$$c_v = \frac{R}{J(k - 1)} \quad (9:18)$$

*Example 9:3A.* During a certain adiabatic process, an air system weighing 3 lb changes from  $p_1 = 100$  psia,  $t_1 = 200^\circ\text{F}$ , to  $p_2 = 20$  psia,  $t_2 = -43^\circ\text{F}$ . Assuming air to be a perfect gas, calculate (a) the change of internal energy of the system, (b) the change of enthalpy, and (c) the external work that accompanied the process.

*Solution:*

$$(a) \quad U_2 - U_1 = Mc_v(T_2 - T_1) = (3)(0.171)(417 - 660) = -124.7 \text{ Btu}$$

$$(b) \quad H_2 - H_1 = Mc_p(T_2 - T_1) = k(U_2 - U_1) = (1.4)(-124.7) = -174.6 \text{ Btu}$$

$$(c) \quad {}_1Q_2 = 0 = U_2 - U_1 + \frac{{}_1W_2}{J} \quad \text{or} \quad {}_1W_2 = -J(U_2 - U_1) = (-778)(-124.7) \\ = 97,000 \text{ ft-lb}$$

*Example 9:3B.* Calculate  $c_p$  and  $c_v$  for methane if  $k = 1.31$  and it is assumed to be a perfect gas.



*Solution.* In Example 9:2B,  $R$  was calculated for methane as 96.4.

$$c_p = \frac{kR}{J(k-1)} = \frac{(1.31)(96.4)}{(778)(0.31)} = 0.525 \text{ Btu/(lb)(}^\circ\text{F)}$$

$$c_v = \frac{c_p}{k} = \frac{0.525}{1.31} = 0.401 \text{ Btu/(lb)(}^\circ\text{F)}$$

**9:4. The Ratio of the Specific Heats.** Equation (9-16) indicates that the difference between the specific heats of a perfect gas is constant. The ratio of the specific heats,  $k$ , can therefore be constant only if  $c_p$  and  $c_v$  are themselves constant. That this is the case for the monatomic perfect gas, where molecular motion is translational only, is proved below.

From Eq. (9:4),

$$Pv = \frac{\bar{V}^2}{3}$$

and, from Eq. (9:7),

$$Pv = RT$$

Therefore

$$\frac{\bar{V}^2}{3} = RT$$

The kinetic molecular energy is, for unit mass,  $\bar{V}^2/2$ . This is the total internal energy of the perfect-gas system of unit mass, or

$$u = \frac{\bar{V}^2}{2J} = \frac{3RT}{2J} \quad (9:19)$$

Differentiating,

$$c_v = \frac{du}{dT} = \frac{3}{2} \frac{R}{J} \quad (9:20)$$

From Eq. (9:16),

$$c_p = c_v + \frac{R}{J} = \frac{5}{2} \frac{R}{J} \quad (9:21)$$

and

$$k = \frac{c_p}{c_v} = \frac{5}{3} \quad (9:22)$$

The value of  $c_v$  stated in Eq. (9:20) and the value of  $k$  given in Eq. (9:22) are approached by all gases, whether monatomic or polyatomic, as their temperature approaches absolute zero, since, at these levels of temperatures, rotational and vibrational kinetic energy vanish. At slightly higher temperatures, rotational energy begins to appear and, at temperatures still well below atmospheric levels, reaches its maximum amount. When this condition has been attained, the rate of storage of internal energy with respect to temperature is increased above that due to changes

in translational kinetic energy alone and stated in Eq. (9:20). It is a principle of quantum mechanics that the total kinetic energy will be in direct proportion to the number of degrees of freedom of motion of the system (in this case, the molecule). When the rotational kinetic energy of a two-atom (diatomic) molecule has been fully excited, the molecule adds two additional degrees of freedom of motion to its three degrees of freedom of translational motion, since it may store energy in significant amount due to rotation about either of two axes perpendicular to each other and to the line joining the two atoms. This makes a total of five degrees of freedom of motion, and the rate of change of internal energy of the perfect gas with respect to temperature in this range of temperature (before vibrational kinetic energy makes its appearance in appreciable degree) is five-thirds as large as when translational kinetic energy was alone involved. Thus, for the diatomic perfect gas in this range,

$$c_v = \frac{5}{2} \left( \frac{3R}{2J} \right) = \frac{5}{2} \frac{R}{J} \quad c_p = c_v + \frac{R}{J} = \frac{7}{2} \frac{R}{J} \quad k = \frac{c_p}{c_v} = \frac{7}{5} \quad (9:23)$$

At temperatures approximating those of the atmosphere, vibrational kinetic energy begins to make its appearance in appreciable amount. This motion accounts for still two more degrees of freedom, and, for the diatomic molecule in which vibrational movement of the atoms has been fully developed,

$$c_v = \frac{7}{2} \frac{R}{J} \quad c_p = \frac{9}{2} \frac{R}{J} \quad k = \frac{9}{7} \quad (9:24)$$

Equations (9:24) state the highest values of  $c_p$  and  $c_v$  (and the lowest value of  $k$ ) theoretically possible for the diatomic perfect-gas molecule. The change from the values shown in Eqs. (9:23) to those of Eqs. (9:24) is gradual and begins to make its appearance at about atmospheric temperature. Calculations based on spectroscopic data for real diatomic gases,<sup>1</sup> such as O<sub>2</sub> and N<sub>2</sub>, seems to show that  $c_p$  may, at temperatures around 9000°R, somewhat exceed the maximum as stated in Eq. (9:24) if  $R$  is calculated as for a perfect gas.

If it is assumed that vibrational kinetic energy has not yet made its appearance, a triatomic molecule may have three degrees of rotational in addition to three degrees of translational freedom. Thus, at about atmospheric levels of temperature, we should expect to find

$$c_v = \frac{6}{2} \frac{R}{J} \quad c_p = \frac{8}{2} \frac{R}{J} \quad k = \frac{8}{6} = 1.33 \quad (9:25)$$

Observed values of  $k$  at these temperature levels are often somewhat less

<sup>1</sup> R. L. Sweigert and M. W. Beardsley, "Empirical Specific Heat Equations Based on Spectroscopic Data," *Georgia School Technol., State Eng. Expt. Sta., Bull.* 1 (No. 3) (1938).



than this theoretical maximum for triatomic gases such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and, ignoring the difference between these gases and their perfect-gas equivalents, we may account for this variation as due to the accumulation of vibrational energy in some degree, even at atmospheric temperature.

It will be remembered (see Art. 9:1) that the concept of the perfect gas was introduced to simplify the calculation of the effects produced during the processes which make up the gas cycle. These calculations then would be, in effect, *approximate* calculations to apply to the real gas. They may be still further simplified if it is assumed that the specific heats of the perfect gas, which is substituted for the real gas, are constant. This will be very nearly the case over the rather wide range of temperature between the temperature at which rotational energy is fully developed and that at which vibrational energy begins to be important; this second level starts at about atmospheric temperature. Accordingly, we shall use, as constants, the values of the specific heats at atmospheric levels of temperature in the calculations to follow.

*Example 9:4.* (a) Helium is a monatomic gas, having a molecular weight of 4.002. Assuming it to be a perfect gas, calculate  $c_p$  and  $c_v$ . (b) Check the values of  $c_p$  and  $c_v$  shown in Table 9:1 for carbon monoxide, assuming it to be a perfect gas.

*Solution:*

(a) As a monatomic gas, the value of  $k$  is  $\frac{5}{3}$  for helium.

$$c_p = \frac{kR}{J(k-1)} = \frac{(5)(1545)}{(778)(2)(4.002)} = 1.24 \text{ Btu/(lb)(}^\circ\text{F)}$$

$$c_v = \frac{c_p}{k} = 0.745 \text{ Btu/(lb)(}^\circ\text{F)}$$

(b) The tabulated values are at atmospheric temperature. This is a diatomic gas, and, assuming that rotational energy is fully developed and vibrational energy is negligible,  $k = \frac{7}{5}$  [see Eq. (9:23)]. Then

$$c_p = \frac{7}{2} \frac{R}{J} = \frac{(7)(1545)}{(2)(778)(28)} = 0.248 \text{ Btu/(lb)(}^\circ\text{F)}$$

$$c_v = \frac{c_p}{k} = \frac{0.248}{1.4} = 0.177 \text{ Btu/(lb)(}^\circ\text{F)}$$

**9:5. Reversible Nonflow Processes.** It is customary to classify reversible processes for the perfect gas according to the value of the constant exponent  $n$  in the pressure-volume relation

$$PV^n = C \quad (9:26)$$

This is done since, as will develop later, if  $c_v$  (and, consequently,  $c_p$ ) for the perfect gas is constant, the amount of heat flow that accompanies a unit change of temperature is the same over every stage of the process. This also accounts for the name, *polytropic process*, which is applied to any reversible process of the perfect gas that can be expressed in the form of Eq. (9:26); the adjective *polytropic*, freely translated, means “at

constant specific heat." To symbolize this constant specific heat we shall use the character  $c_n$ , representing the heat flow in Btu that accompanies an increase in temperature of  $1^\circ\text{F}$  per pound of system weight.

From Eq. (2:3),  ${}_1Q_2 - {}_1W_2/J = U_2 - U_1$ . Assuming, for the moment, that  $c_n$  is constant during the polytropic perfect-gas process to which we expect to apply this equation,

$${}_1Q_2 = Mc_n(T_2 - T_1) \quad (9:27)$$

Based on Eq. (2:6), and since  $P = C/V^n$  in Eq. (9:26),

$$\begin{aligned} {}_1W_2 &= \int_{V_1}^{V_2} P dV = C \int_{V_1}^{V_2} \frac{dV}{V^n} = C \left[ \frac{V^{-n+1}}{-n+1} \right]_{V_1}^{V_2} \\ &= \frac{C}{1-n} (V_2^{1-n} - V_1^{1-n}) \end{aligned}$$

or since  $C = PV^n = P_1V_1^n = P_2V_2^n$ ,

$${}_1W_2 = \frac{P_2V_2^nV_2^{1-n} - P_1V_1^nV_1^{1-n}}{1-n} = \frac{P_1V_1 - P_2V_2}{n-1} \quad (9:28)$$

Alternately, since  $P_1V_1 = MRT_1$  and  $P_2V_2 = MRT_2$ , if the system is a perfect gas,

$${}_1W_2 = \frac{MR}{n-1} (T_1 - T_2) \quad (9:29)$$

From Eq. (9:14), if  $c_v$  is constant,

$$U_2 - U_1 = Mc_v(T_2 - T_1) \quad (9:30)$$

Substituting the expressions obtained from Eqs. (9:27), (9:29), and (9:30) in Eq. (2:3) and rearranging,

$$Mc_n(T_2 - T_1) = Mc_v(T_2 - T_1) - \frac{MR}{J(n-1)} (T_2 - T_1) \quad (9:31)$$

or, dividing by  $M(T_2 - T_1)$  and applying Eq. (9:18),

$$c_n = c_v - \frac{R}{J(n-1)} = c_v \left( 1 - \frac{k-1}{n-1} \right) = c_v \frac{n-k}{n-1} \quad (9:32)$$

Since  $n$  is constant by definition and  $k$  is constant if, as was assumed,  $c_v$  and  $c_p$  are constants,  $c_n$  is a constant and the term polytropic, as applied to the process, is justified.

The relations between the heat flow, the change of internal energy, and the external work of a perfect-gas system during a reversible polytropic process may be obtained by comparing their values as expressed in Eqs. (9:27) to (9:30). For example,

$$\frac{{}_1Q_2}{U_2 - U_1} = \frac{c_n}{c_v} = \frac{n-k}{n-1} \quad (9:33)$$



Similarly,

$$\frac{J {}_1Q_2}{{}_1W_2} = \frac{Jc_n(n-1)}{-R} = -\frac{(n-k)(k-1)}{n-1} \quad (9:34)$$

and

$$\frac{J(U_2 - U_1)}{{}_1W_2} = \frac{Jc_v(n-1)}{-R} = -\frac{n-1}{k-1} \quad (9:35)$$

For the polytropic,  $\partial Q$  is  $Mc_n dT$  [the differential form of Eq. (9:27)], and

$$S_2 - S_1 = \int_1^2 \frac{\partial Q}{T} = Mc_n \int_{T_1}^{T_2} \frac{dT}{T} = Mc_n \log_e \frac{T_2}{T_1} = Mc_v \frac{n-k}{n-1} \log_e \frac{T_2}{T_1} \quad (9:36)$$

The reversible polytropic is the general form which fits all perfect gases with constant  $c_v$  to give a process for which the ratio of heat flow to temperature change is constant. The reversible constant-pressure, constant-volume, isothermal, constant-internal-energy, and adiabatic processes discussed in Chap. 2 are special cases of the polytropic, each distinguished by a special value of the constant exponent  $n$  and a corresponding constant value of  $c_n$ . For the constant-pressure process,  $P = C$ , which may be written as  $PV^0 = C$ , and the value of  $n$  is therefore zero. The constant-volume process,  $V = C$ , becomes  $P^0V = C$ , or  $P^{1/\infty}V = C$ , and, raising this to the infinite power, we have  $PV^\infty = C^\infty$ , where  $C^\infty$  is still a constant;  $n$  for the constant-volume process is  $\infty$ . The isothermal, or constant-temperature, process follows Boyle's law and is stated as  $PV = C$ , so that  $n$  is 1; from Joule's law, the same value of  $n$  will also apply to the constant-internal-energy process. The reversible adiabatic involves no heat flow, and  $c_n$  is therefore zero. But  $c_n = c_v(n-k)/(n-1)$  and since  $c_v$  cannot be zero (except at the absolute zero of temperature),  $(n-k)/(n-1) = 0$ , or  $n = k = c_p/c_v$ . The equation of the reversible adiabatic for the perfect-gas system is therefore

$$PV^k = C \quad (9:37)$$

*Example 9:5A.* Show, by applying the nonflow energy equation to a perfect gas, that  $n = k$  for a reversible adiabatic (isentropic) process.

*Solution:*

$$\partial Q - \frac{\partial W}{J} = dU \quad [\text{Eq. (2:5)}]$$

But  $\partial Q = 0$  if the process is adiabatic, and, if reversible,  $\partial W = P dV$ . Thus

$$0 = dU + \frac{P dV}{J} = Mc_v dT + \frac{P dV}{J}$$

For a perfect gas,  $PV = MRT$ , and, differentiating,  $P dV + V dP = MR dT$ . Solving for  $dT = \frac{P dV}{MR} + \frac{V dP}{MR}$  and substituting in the preceding equation,

$$\frac{c_v P dV}{R} + \frac{c_v V dP}{R} + \frac{P dV}{J} = 0$$

or, assembling coefficients of  $dV$ ,

$$\left(\frac{c_v}{R} + \frac{1}{J}\right) P dV + \left(\frac{c_v}{R}\right) V dP = 0$$

Multiplying by  $R$ ,

$$\left(c_v + \frac{R}{J}\right) P dV + c_v V dP = c_p P dV + c_v V dP = 0$$

Separating the variables by dividing by  $PV$ ,

$$c_p \frac{dV}{V} + c_v \frac{dP}{P} = 0 \text{ or } \frac{k dV}{V} + \frac{dP}{P} = 0$$

Integrating,

$$k \log_e V + \log_e P = C \text{ (constant of integration)}$$

This relation may be expressed as  $PV^k = C$ , where  $C$  is a new constant equal to  $P_1 V_1^k$ .

The family of polytropics may be traced on a  $PV$  chart as in Fig. 9:3.

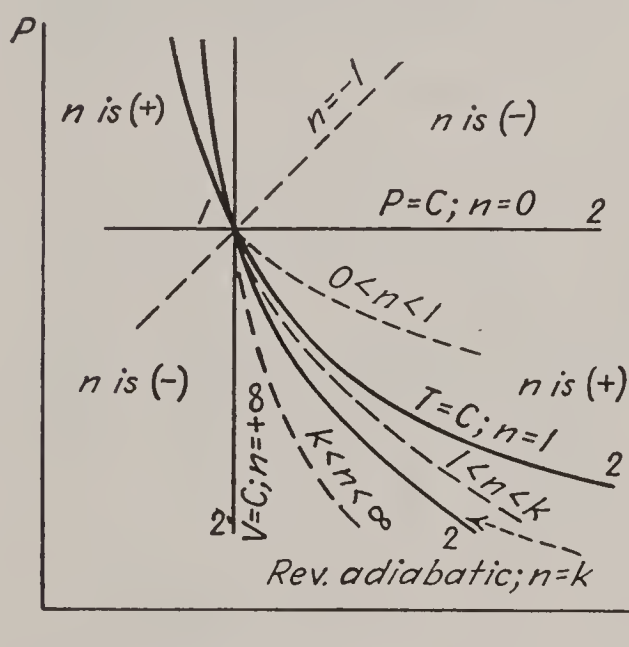


FIG. 9:3. Polytropic processes on the  $PV$  chart.

For positive values of  $n$ , the curves lie in the second and fourth quadrants, if the common initial state 1 for all processes is used as the origin, and these quadrants include all the more usual processes. When the rate of heat and/or work flow is large enough so that the pressure and volume may increase or decrease together (a condition seldom encountered in practice), the value of  $n$  will be negative and the curves will lie in the first and third quadrants.

The equation of state  $Pv = RT$  and the polytropic relation  $Pv^n = C$  may be used to determine the  $PvT$  relationships between two states that lie on the same polytropic. From the first,

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \quad \text{or} \quad \frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 v_1} \quad (9:38)$$

and, from the second,

$$\frac{P_1}{P_2} = \left(\frac{v_2}{v_1}\right)^n \quad \text{or} \quad \frac{v_1}{v_2} = \left(\frac{P_2}{P_1}\right)^{1/n} \quad (9:39)$$



Combining Eqs. (9:38) and (9:39),

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(n-1)/n} \quad (9:40)$$

The appearance of the perfect-gas polytropics on the temperature-entropy diagram is shown in Fig. 9:4. A discussion of the method of location of the constant-volume, constant-pressure, isothermal, and reversible adiabatic paths on this diagram will be found in Chap. 6. The direction 1-2 on these curves corresponds to increasing volume or, in the case of the constant-volume path, to decreasing pressure.

The substitution of the proper value of  $n$  in Eqs. (9:26) to (9:40) leads directly to the information tabulated in Table 9:2 except in the case of the isothermal process; for this process, the heat flow, the work, and the change of entropy are indeterminate from these equations. But the change of internal energy accompanying this process is zero for

a perfect gas according to Joule's law, and, by Eq. (2:3), the heat flow must equal the work of the reversible process. The equation of the path is  $PV = C = P_1V_1 = MRT$ , or  $P = C/V = P_1V_1/V = MRT/V$ . Thus the work may be calculated as

$${}_1W_2 = \int_1^2 P dV = P_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = P_1V_1 \log_e \frac{V_2}{V_1} = MRT \log_e \frac{V_2}{V_1} \quad (9:41)$$

and the heat flow is

$${}_1Q_2 = \frac{{}_1W_2}{J} = \frac{P_1V_1}{J} \log_e \frac{V_2}{V_1} = \frac{MRT}{J} \log_e \frac{V_2}{V_1} \quad (9:42)$$

This heat flow is represented by the rectangular area under the  $n = 1$  curve of Fig. 9:4, and the change of entropy is therefore

$$S_2 - S_1 = \frac{{}_1Q_2}{T} = \frac{P_1V_1}{JT} \log_e \frac{V_2}{V_1} = \frac{MR}{J} \log_e \frac{V_2}{V_1} \quad (9:43)$$

Table 9:2 will be found convenient for reference in the solution of problems concerned with nonflow reversible processes of perfect-gas systems for which  $c_v$  has a constant value.

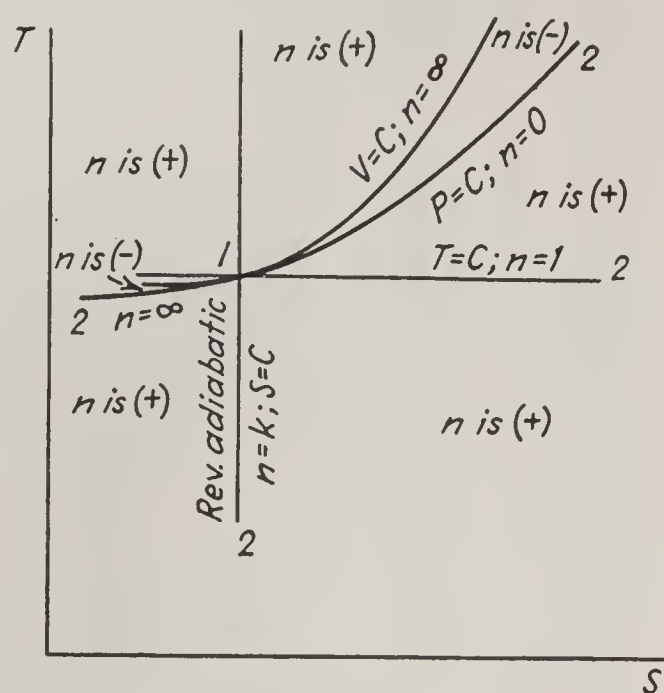


FIG. 9:4. Polytropic processes on the  $TS$  chart.

TABLE 9.2. SUMMARY OF NONFLOW REVERSIBLE PROCESSES FOR PERFECT-GAS SYSTEMS

$c_v$  constant

Type of process	Value of exponent $n$	Final pressure $P_2$	Final temperature $T_2$	Final volume $V_2$	Heat supplied system ${}_1Q_2$	Change of internal energy of system $U_2 - U_1$	Work performed by system ${}_1W_2$	Change of entropy of system $S_2 - S_1$
Constant pressure	0	$P_1$	$T_1 \frac{V_2}{V_1}$	$\frac{T_2}{T_1} \frac{V_2}{V_1}$	$M c_p (T_2 - T_1)$	$M c_v (T_2 - T_1)$ or $\frac{P_2 V_2 - P_1 V_1}{J(k - 1)}$	$P(V_2 - V_1)$	$M c_p \log_e \frac{T_2}{T_1}$ or $M c_p \log_e \frac{V_2}{V_1}$
Constant volume	$\infty$	$P_1 \frac{T_2}{T_1}$	$T_1 \frac{P_2}{P_1}$	$V_1$	$M c_v (T_2 - T_1)$	$M c_v (T_2 - T_1)$ or $\frac{P_2 V_2 - P_1 V_1}{J(k - 1)}$	0	$M c_v \log_e \frac{T_2}{T_1}$ or $M c_v \log_e \frac{P_2}{P_1}$
Isothermal-constant temperature	1	$P_1 \frac{V_1}{V_2}$	$T_1$	$\frac{P_1}{V_1} \frac{V_2}{P_2}$	$\frac{P_1 V_1}{J} \log_e \frac{V_2}{V_1}$	0	$P_1 V_1 \log_e \frac{V_2}{V_1}$	$\frac{MR}{J} \log_e \frac{V_2}{V_1}$ or $\frac{MR}{J} \log_e \frac{P_1}{P_2}$
Reversible adiabatic-isentropic	$k$	$P_1 \left( \frac{V_1}{V_2} \right)^k$ or $P_1 \left( \frac{T_2}{T_1} \right)^{k/(k-1)}$	$T_1 \left( \frac{V_1}{V_2} \right)^{k-1}$ or $T_1 \left( \frac{P_2}{P_1} \right)^{(k-1)/k}$	$V_1 \left( \frac{P_1}{P_2} \right)^{1/k}$ or $V_1 \left( \frac{T_1}{T_2} \right)^{1/(k-1)}$	0	$M c_v (T_2 - T_1)$ or $\frac{P_2 V_2 - P_1 V_1}{J(k - 1)}$	$J M c_v (T_1 - T_2)$ or $\frac{P_1 V_1 - P_2 V_2}{k - 1}$	0
Polytropic	Any constant value	$P_1 \left( \frac{V_1}{V_2} \right)^n$ or $P_1 \left( \frac{T_2}{T_1} \right)^{n/(n-1)}$	$T_1 \left( \frac{V_1}{V_2} \right)^{n-1}$ or $T_1 \left( \frac{P_2}{P_1} \right)^{(n-1)/n}$	$V_1 \left( \frac{P_1}{P_2} \right)^{1/n}$ or $V_1 \left( \frac{T_1}{T_2} \right)^{1/(n-1)}$	$M c_v \frac{n - k}{n - 1} (T_2 - T_1)$	$M c_v (T_2 - T_1)$ or $\frac{P_2 V_2 - P_1 V_1}{J(k - 1)}$	$\frac{MR(T_1 - T_2)}{(n - 1)}$ or $\frac{P_1 V_1 - P_2 V_2}{n - 1}$	$M c_v \frac{n - k}{n - 1} \log_e \frac{T_2}{T_1}$

\*  $MRT$  may be substituted for  $P_1 V_1$  or  $P_1/P_2$  for  $V_2/V_1$  if more convenient.  
†  $(V_1/V_2)^{n-1}$  or  $(P_1/P_2)^{(n-1)/n}$  may be substituted for  $T_2/T_1$  if more convenient.



**Example 9:5B.** As the result of a polytropic (reversible) process, a 3-lb air system changes from 100 psia, 200°F, to 20 psia, 0°F. Calculate (a) the change of internal energy, (b) the heat flow, (c) the external work, (d) the change of enthalpy, and (e) the change of entropy that accompany the process. Consider the system to be a perfect gas with constant specific heats,  $c_p$  and  $c_v$ .

*Solution:*

$$(a) U_2 - U_1 = Mc_v(T_2 - T_1) = (3)(0.171)(460 - 660) = -102.6 \text{ Btu}$$

(b) From Eq. (9:40),

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(n-1)/n} \text{ or } \frac{460}{660} = \left(\frac{20}{100}\right)^{(n-1)/n}$$

Thus

$$\frac{n-1}{n} = \frac{\log \frac{460}{660}}{\log \frac{20}{100}} = \frac{-0.362}{-1.61} = 0.225 \text{ and } n = 1.29$$

$$c_n = c_v \frac{n-k}{n-1} = 0.171 \left( \frac{1.29-1.4}{1.29-1} \right) = -0.065$$

$${}_1Q_2 = Mc_n(T_2 - T_1) = (3)(-0.065)(-200) = 39.0 \text{ Btu}$$

$$(c) {}_1W_2 = \frac{MR(T_1 - T_2)}{n-1} = \frac{(3)(53.3)(200)}{0.29} = 110,000 \text{ ft-lb}$$

Checking,

$${}_1W_2 = J({}_1Q_2 - \Delta U) = 778(39.0 + 102.6) = 110,000 \text{ ft-lb}$$

$$(d) H_2 - H_1 = Mc_p(T_2 - T_1) = (3)(0.240)(-200) = -144 \text{ Btu}$$

$$(e) S_2 - S_1 = Mc_n \log_e \frac{T_2}{T_1} = (3)(-0.065) \log_e \frac{460}{660} = (3)(-0.065)(-0.362) = 0.071$$

**9:6. The Irreversible Nonflow Process.** Even if  $n$  has a constant value in the equation  $PV^n = C$ , that equation does not necessarily represent a polytropic unless the process is a limiting (reversible) process, and the information contained in Table 9:2 cannot be applied to the calculation of either the heat flow or the work that accompanies the process. Heat and work have been shown to have maximum values (in the algebraic sense) for the reversible process. As applied to the adiabatic process, for example, the reversible process has been shown to have a value of  $n$  equal to the ratio of the specific heats, or  $k$ . If, owing to the effects of factors such as friction or unrestrained expansion, the work accompanying an adiabatic expansion were reduced to zero (see Chap. 2), the process would take place at constant internal energy and  $n$  would be 1 for the perfect-gas system. Even this is not a limiting case, for it is conceivable that the work might even be negative and  $n$  thus less than 1. The value of  $n$  during an irreversible adiabatic for a perfect gas must be less than  $k$ , the deviation from that value depending on the amount of irreversibility.

Although a constant value of  $n$  during an irreversible process for a perfect gas does not stamp the process as a polytropic or fix the values of work

or heat flow, it does establish the series of states through which the system has passed and the corresponding change in properties such as the internal energy, enthalpy, and entropy. Also, although their individual values are not calculable, the difference between the heat flow and the work may be determined. This is true, of course, even if  $n$  is not constant over the path connecting the initial and final states of the system. In fact, the path need not be known, and the calculation may be based on the end states alone. If the path is known, limiting values of the work and the heat flow are established and these values cannot be exceeded for any process that follows the same path.

*Example 9:6.* Assume, in Example 9:5B, that the same system follows the same path but as the result of an irreversible adiabatic process. Find the same quantities as in Example 9:5B.

*Solution.* The internal energy, the enthalpy, and the entropy are properties, and their changes depend only on the end states, which are the same for the irreversible as for the reversible process of Example 9:5B. The answers to parts *a*, *d*, and *e* are therefore the same as in that example. The heat flow is, according to the description of the irreversible process as an adiabatic, zero. The work may be calculated from Eq. (2:3) as

$${}_1W_2 = J({}_1Q_2 - \Delta U) = 778[0 - (-102.6)] = 79,800 \text{ ft-lb}$$

It will be noted that this amount of work is less than the maximum work (110,000 ft-lb) that is associated with the reversible process. Also observe that the value of  $n$  (1.29) is less than  $k$  for this gas.

**9:7. Changes of Entropy.** In Table 9:2 are given the changes of entropy over reversible polytropic processes connecting an initial state 1 with a final state 2. It was shown in Chap. 6 that this change of entropy was the same for the same end states regardless of the process, reversible or irreversible, that connected them and could be *calculated* as  $\int_1^2 \frac{\partial Q}{T}$  over any *reversible* process or processes that joined the two states; this was the basis of Eq. (6:8). Starting with that equation, we may write, for the perfect-gas system,

$$dS = \frac{dU}{T} + \frac{P dV}{JT} = \frac{Mc_v dT}{T} + \frac{MR dV}{JV} \quad (9:44)$$

$$= \frac{Mc_v d(PV)}{PV} + \frac{MR dV}{JV} \quad (9:45)$$

$$= \frac{Mc_p dV}{V} + \frac{Mc_v dP}{P} \quad (9:46)$$

$$= \frac{Mc_p dT}{T} - \frac{MR dP}{JP} \quad (9:47)$$

Integration between the limits determined by the properties at states 1 and 2 gives, respectively,



$$S_2 - S_1 = Mc_v \log_e \frac{T_2}{T_1} + \frac{MR}{J} \log_e \frac{V_2}{V_1} \quad (9:44a)$$

$$= Mc_v \log_e \frac{P_2 V_2}{P_1 V_1} + \frac{MR}{J} \log_e \frac{V_2}{V_1} \quad (9:45a)$$

$$= Mc_p \log_e \frac{V_2}{V_1} + Mc_v \log_e \frac{P_2}{P_1} \quad (9:46a)$$

$$= Mc_p \log_e \frac{T_2}{T_1} - \frac{MR}{J} \log_e \frac{P_2}{P_1} \quad (9:47a)$$

Equations (9:44a) to (9:47a) will be found convenient when the difference of entropy between two known states is to be calculated without any knowledge of what single reversible polytropic would connect these states. They assume that the change of state is accomplished in two reversible steps and add the individual changes of entropy of these two segments to obtain the total change. For example, in Eq. (9:44a), the two segments are, respectively, at constant volume and at constant temperature. An alternate method would consist in solving for  $n$  in Eq. (9:39) or (9:40) and then applying the appropriate equation from Table 9:2 as in Example 9:5B.

*Example 9:7.* Calculate the change of entropy in Example 9:5B by selecting and applying a suitable equation from Eqs. (9:44a) to (9:47a). Compare with the value previously calculated.

*Solution.* The initial and final pressures and temperatures being given, it will be convenient to make use of Eq. (9:47a). Then

$$\begin{aligned} S_2 - S_1 &= Mc_p \log_e \frac{T_2}{T_1} - \frac{MR}{J} \log_e \frac{P_2}{P_1} = (3)(0.240)(-0.362) - \frac{(3)(53.3)(-1.61)}{778} \\ &= -0.261 + 0.332 = 0.071 \end{aligned}$$

This agrees with the value as calculated in Example 9:5B.

**9:8. The Steady-flow Process.** Equation (3:5) may be written

$${}_1Q_2 - \frac{{}_1W_2}{J} = h_2 - h_1 + \frac{\Delta(\bar{V}^2)}{2Jg} + \frac{\Delta z}{J}$$

and, for the change of enthalpy,  $h_2 - h_1$ , as it applies to a perfect gas, we may substitute

$$\begin{aligned} h_2 - h_1 &= c_p(T_2 - T_1) = k(u_2 - u_1) = \frac{k}{k-1} \frac{P_2 v_2 - P_1 v_1}{J} \\ &= \frac{kP_1 v_1}{(k-1)J} \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \quad (9:48) \end{aligned}$$

If the steady-flow process is reversible and adiabatic, with negligible changes in kinetic energy and elevation,  $n = k$  and

$${}_1W_2 = (h_1 - h_2)J = \frac{k}{k-1} P_1 v_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \quad (9:49)$$

To deal with the more general case where the steady-flow process, though polytropic (reversible with  $n$  constant), is not adiabatic, we may write the energy equation for steady flow, again assuming negligible change in kinetic energy and elevation, in differential form as

$$\partial Q - \frac{\partial W}{J} = dh = d\left(u + \frac{Pv}{J}\right) = du + \frac{P dv}{J} + \frac{v dP}{J} = \partial Q + \frac{v dP}{J}$$

and note that  $\partial W = -v dP$ . For the polytropic,  $Pv^n = C = P_1v_1^n = P_2v_2^n$ , and  $v = P_1^{1/n}v_1/P^{1/n} = P_2^{1/n}v_2/P^{1/n}$ . Therefore, for the reversible steady-flow polytropic process,

$$\begin{aligned} ({}_1W_2)_{\text{rev, steady flow}} &= - \int_1^2 v dP = -P_1^{1/n}v_1 \int_{P_1}^{P_2} \frac{dP}{P^{1/n}} \\ &= P_1^{1/n}v_1 \left( \frac{n}{n-1} \right) (P_1^{(n-1)/n} - P_2^{(n-1)/n}) \\ &= \frac{n}{n-1} (P_1v_1 - P_2v_2) = \frac{n}{n-1} P_1v_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(n-1)/n} \right] \end{aligned} \quad (9:50)$$

It will be noted that Eq. (9:49) is a special case of Eq. (9:50).

When the steady-flow process is isothermal,  $n = 1$  and Eq. (9:50) yields an indeterminate result. Returning to  $\partial W = -v dP$ , however, and substituting  $v = P_1v_1/P$ , we obtain, for the *reversible isothermal steady-flow process*,

$${}_1W_2 = - \int_1^2 v dP = -P_1v_1 \int_{P_1}^{P_2} \frac{dP}{P} = P_1v_1 \log_e \frac{P_1}{P_2} \quad (9:51)$$

**9:9. The continuous compression of gases** is frequently necessary in the course of engineering operations. This may be accomplished by apparatus such as fans, blowers, or reciprocating compressors, the chief thermodynamic distinction between these devices being found in the differential of pressure which they create. In general, the reciprocating compressor is associated with the larger differentials of pressure and will therefore be used as the basis of our discussion. Although the flow is quasi-steady (see Art. 3:9) to at least some degree in all these devices, Eqs. (9:49) to (9:51) may be used to obtain the work required for the compression of unit weight if an equivalent perfect gas is substituted for the real gas and if the processes making up the cycle of operation are idealized as reversible processes. The equations will show this work to be negative, indicating that it must be supplied by some external agency. By taking into account the rate at which the gas is compressed, the ideal (minimum, or theoretical) power required to drive the compressor may be calculated.

The principle of operation of the reciprocating air compressor is shown in Figs. 9:5 and 9:6. The compressor is shown, for simplicity, as single-



acting although valves at both ends of the cylinder would approximately double its capacity at the same speed. Both intake and exhaust valves are usually automatic in their action, being opened and closed by differences in the air pressure acting on their opposite faces; when the pressures are balanced, they are kept closed by light springs (not shown in the figure). In operation, the pressure of the atmosphere acts on the outside of the intake valve; that of the air at receiver (discharge) pressure on the outside of the discharge valve. Thus, if the pressure within the cylinder is caused to fall below atmospheric pressure by an amount sufficient to overcome the small resistance offered by the valve spring plus the resistance to flow offered by the intake passage, the intake valve will open and

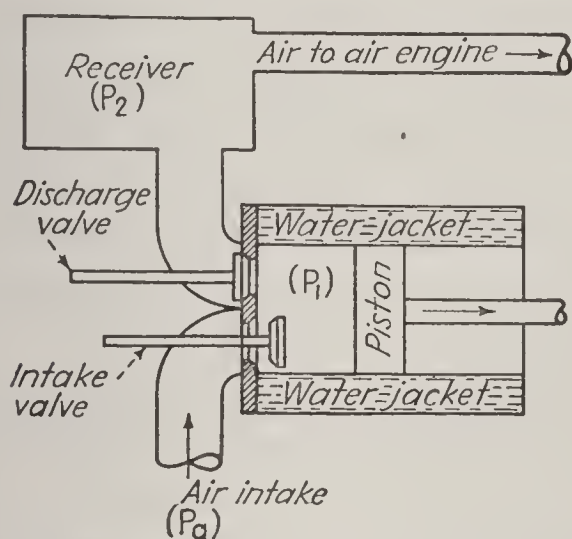


FIG. 9:5. Piston air compressor.

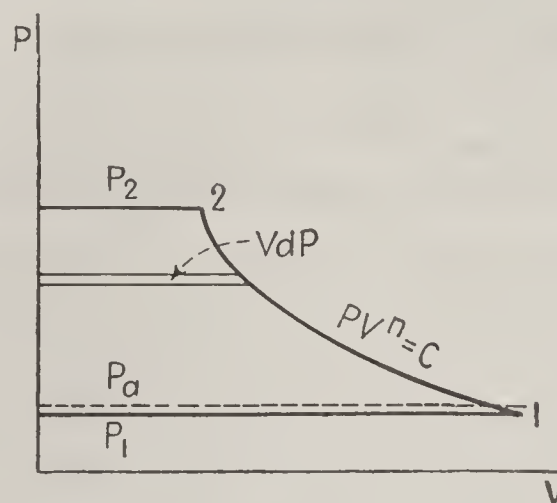


FIG. 9:6. Cycle of an air compressor.

air will be drawn from the atmosphere into the cylinder. Similarly, if, as the result of piston action, the pressure of the charge within the cylinder reaches a value sufficiently above the receiver pressure to overcome the resistance of the spring on the discharge valve plus exhaust-passage resistance, this valve will open and discharge will take place from the cylinder into the receiver.

In the position shown, the piston is moving to the right on its *suction* stroke. Referring to the  $PV$  diagram (Fig. 9:6), which has been drawn for a compressor with no clearance, a charge of air will be drawn into the cylinder at constant pressure  $P_1$ ; this pressure, as explained above, will be slightly below that of the atmosphere from which the flow takes place, and atmospheric pressure is shown as a dashed line on the diagram.

At point 1, the piston reaches the end of its suction stroke and reverses the direction of its motion. The intake valve closes immediately, since the pressure in the cylinder is no longer low enough to keep it open, and *compression* of the charge proceeds along the line 1-2. At point 2, the pressure  $P_2$  within the cylinder has become slightly higher than the receiver pressure, and this differential of pressure is sufficient to open the discharge valve; the remainder of the stroke of the piston as it continues to move to the left is concerned with the *delivery* of the compressed charge

to the receiver. As the piston reaches the left end of the cylinder and again starts on its suction stroke, it will be observed that the discharge valve will close, the intake valve will open, in response to the lowered pressure within the cylinder, and the cycle of operation of the compressor will have been completed.

Figure 9:6 is a theoretical indicator diagram for the air compressor with no clearance. The drop in pressure from  $P_a$  to  $P_1$  across the intake valve is the effect of a throttling process, adiabatic (though not frictionless and therefore not isentropic) and with no external work. Considering the differences of kinetic energy and elevation to be negligible,  $h_1 = h_a$  or, handling the air as a perfect gas,  $T_1 = T_a$ . The enclosed area of this diagram measures the work required for the cyclic compression of a unit weight of the gas if the volume at point 1 is  $v_1$ , the specific volume at  $P_1$  and  $T_1 (= T_a)$ . As indicated on the figure, this area is the summation of the slices  $V dP$  (for unit weight,  $v dP$ ), and since Eqs. (9:49) to (9:51) represent the result of this summation, these equations may be used to measure the work area. The particular equation selected for the purpose will depend on the value of  $n$  over the compression curve 1-2.

If the compression occurs rapidly in an insulated cylinder, it may be assumed to be adiabatic, with  $n = k$ ; if carried out very slowly, with proper provision, such as a water jacket, for the removal of heat from the cylinder, it will approach the isothermal, with  $n = 1$ . If it is assumed that compression begins from atmospheric temperature and that the temperature of the fluid used to cool the cylinder is not below that of the atmosphere, these two values of  $n$  may be regarded as the limiting values for the reversible compression. The value of  $n$  for a water-cooled air compressor will be a compromise between these values and may be expected to lie in the range 1.25 to 1.35. This would correspond, in the compression of a triatomic gas such as carbon dioxide, with  $k = 1.29$ , to a practical value of  $n$  of about 1.2. In the case of an uncooled compressor, such as a blower, the value of  $n$  will exceed  $k$  owing to irreversibilities. The exponent  $n$  is assumed to be constant along the curve 1-2 because of the simplicity of calculation thereby made possible; this does not correspond to the thermodynamic probabilities since, with the difference between cooling-fluid temperature and charge temperature a minimum at the beginning of compression, the heat flow should be very slow during the early stages of process 1-2, with  $n$  approaching  $k$ . Further along, as the temperature differential increased, the rate of heat flow should increase and  $n$  should correspondingly decrease.

Figure 9:7 illustrates the saving of work that results from cooling the compressor cylinder. Curve  $A$  is a  $PV^k = C$  relation and represents adiabatic compression of the charge, curve  $B$  represents isothermal compression, and curve  $C$  is the usual compromise between these limiting



values. The respective cyclic areas show the effect of cooling in reducing the work of cyclic compression. It will be noted that the proportional reduction in this area for isothermal as compared with adiabatic compression increases very rapidly with the pressure ratio,  $P_2/P_1$ . When this pressure ratio is low, as for fans and blowers creating relatively small pressure differentials, cooling becomes less important.

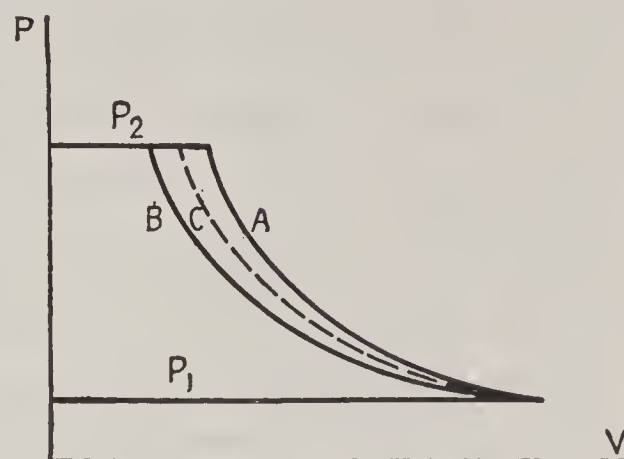


FIG. 9:7. Comparison of adiabatic and isothermal air-compressor diagrams.

*Example 9:9.* Calculate the power theoretically required for the compression of 100 lb of air per minute from 14 psia and 70°F to a final pressure of 350 psia when the compression is (a) adiabatic, (b) isothermal, and (c) when  $n = 1.3$ .

*Solution.* For  $P_1 v_1$  in Eqs. (9:49) to (9:51) may be substituted  $RT_1$ .

(a) For adiabatic compression, using Eq. (9:49),

$$\begin{aligned} \text{Work per min} &= \frac{k}{k-1} MRT_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \\ &= \left( \frac{1.4}{0.4} \right) (100)(53.3)(530) \left[ 1 - \left( \frac{350}{14} \right)^{0.4/1.4} \right] \\ &= 9,900,000(1 - 2.51) = -14,950,000 \text{ ft-lb/min, or 453 hp} \end{aligned}$$

(b) For isothermal compression [Eq. (9:51)],

$$\begin{aligned} \text{Work per min} &= MRT_1 \log_e \frac{P_1}{P_2} = (100)(53.3)(530) \log_e \frac{14}{350} \\ &= (2,830,000)(-3.22) = -8,830,000 \text{ ft-lb/min, or 267 hp} \end{aligned}$$

(c) For polytropic compression with  $n = 1.3$  [Eq. (9:50)],

$$\begin{aligned} \text{Work per min} &= \frac{n}{n-1} MRT_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(n-1)/n} \right] \\ &= \left( \frac{1.3}{0.3} \right) (100)(53.3)(530) \left[ 1 - \left( \frac{350}{14} \right)^{0.3/1.3} \right] \\ &= 12,250,000(1 - 2.105) = -13,500,000 \text{ ft-lb/min, or 410 hp} \end{aligned}$$

For fans and blowers, because of the relatively low pressure differential,  $v_2$  is only very slightly smaller than  $v_1$ . If their cycle of operation is placed on a  $PV$  diagram, the enclosed area is observed to be nearly rectangular and equal, approximately, to  $(P_2 - P_1)V$ . Thus it has become customary to use the following simplified expression for the theoretical power input to such devices:

$$hp = \frac{(P_2 - P_1)V}{33,000} = \frac{\Delta z V}{33,000v} = \frac{M \Delta z}{33,000} \quad (9:52)$$

in which  $V$  = volume of gas handled per minute,  $\text{ft}^3$

$P_2 - P_1$  = differential of pressure created, psf

$\Delta z$  = head of gas equivalent to this pressure difference, ft of gas

$v$  = specific volume of gas,  $\text{ft}^3/\text{lb}$

$M$  = weight of gas handled, lb/min

If  $\Delta z$  is calculated as based on the initial pressure and temperature, the result will be slightly too large and, if based on discharge density, slightly too small; if the differential of pressure is less than 3 per cent of  $P_1$ , the error is usually considered negligible.

**9:10. Multistage Compression.** If the ratio  $P_2/P_1$  exceeds 5, for example, if air is compressed from atmospheric pressure to 75 psia or

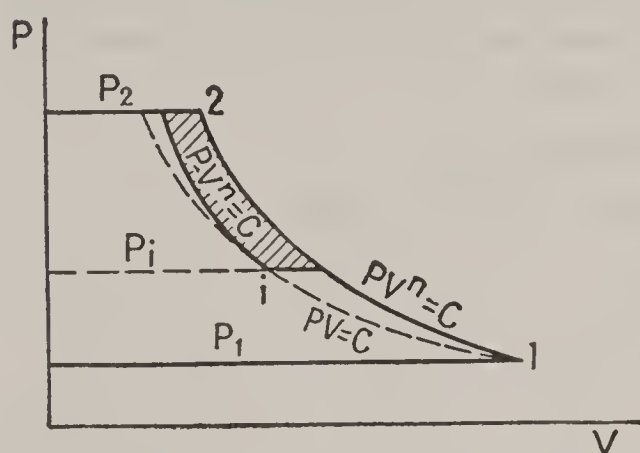


FIG. 9:8. Effect of multistaging in gas compression.

above, the compression is often divided into two or more stages. Receivers are installed between the cylinders in which the successive compressions are effected in order to allow the compressed air to cool to atmospheric temperature before entering the succeeding stage. If the compression could be carried out isothermally, no theoretical advantage would be gained by multistaging. When the compression curve follows the ploytropic

$PV^n = C$ , the saving in work that results from two-stage compression is shown in Fig. 9:8. In the first stage, the air is compressed to an intermediate pressure  $P_i$ , the work per pound being, from Eq. (9:50),

$$W_{\text{1st stage}} = \frac{n}{n-1} P_1 v_1 \left[ 1 - \left( \frac{P_i}{P_1} \right)^{(n-1)/n} \right]$$

In the receiver between the first and second stages, the air is cooled at constant pressure  $P_i$  to atmospheric temperature so that the point  $i$ , from which the second stage of compression starts, lies on an isothermal through point 1, and  $P_i v_i = P_1 v_1$ . The work performed on the air in the second stage, assuming  $n$  to have the same value as in the first stage, is

$$W_{\text{2d stage}} = \frac{n}{n-1} P_1 v_1 \left[ 1 - \left( \frac{P_2}{P_i} \right)^{(n-1)/n} \right]$$

The saving effected over single-stage compression is represented by the crosshatched area. The total work is the (negative) sum of the work areas for the first and the second stages, and this evidently becomes a minimum when the expression

$$\left( \frac{P_i}{P_1} \right)^{(n-1)/n} + \left( \frac{P_2}{P_i} \right)^{(n-1)/n}$$



has its minimum value. If we designate this function of  $P_i$  ( $P_1$  and  $P_2$  are constants since they are fixed as the limiting pressures of the total compression) by the symbol  $G$ , then the value of  $P_i$  obtained when  $dG/dP_i$  equals zero will correspond to the minimum value of the function  $G$  and, therefore, to minimum total work. This mathematical operation shows that, for minimum total work,

$$P_i^2 = P_1 P_2 \quad \text{or} \quad \frac{P_i}{P_1} = \frac{P_2}{P_i} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{2}}$$

It will be noted that this ratio of pressures indicates that, for least total work, the work performed on the gas in the high- and low-pressure cylinders of a two-stage compressor will be equal. An analysis of three-stage compression will indicate that this principle of equal work performance, and therefore of equal pressure ratios for the individual stages, will again prevail, and thus

$$\frac{P'}{P_1} = \frac{P''}{P'} = \frac{P_2}{P''} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{3}}$$

in which  $P'$  and  $P''$  are the absolute pressures at the end of the first and second stages, respectively. Similarly, for any number of compression stages  $X$ , the pressure ratio in each stage for minimum total work will become  $(P_2/P_1)^{1/X}$ . Substituting  $(P_2/P_1)^{1/X}$  for  $P_2/P_1$  in Eq. (9:50), the work per stage may be calculated. But equal work is performed in each of  $X$  stages, and the total work of staged compression between the pressures  $P_1$  and  $P_2$  is

$$W_{X \text{ stages}} = \frac{Xn}{n-1} P_1 v_1 \left[ 1 - \left(\frac{P_2}{P_1}\right)^{(n-1)/Xn} \right] \quad (9:53)$$

*Example 9:10.* Calculate the power theoretically required for the two-stage compression of 100 lb of air per minute from 14 psia, 70°F, to 350 psia when  $n = 1.3$ . Compare with result obtained in part *c* of Example 9:9.

*Solution.* Substituting  $RT_1$  for  $P_1 v_1$  in Eq. (9:53),

$$\begin{aligned} \text{Work per min} &= \frac{Xn}{n-1} M R T_1 \left[ 1 - \left(\frac{P_2}{P_1}\right)^{(n-1)/Xn} \right] \\ &= \left[ \frac{(2)(1.3)}{0.3} \right] (100)(53.3)(530) \left[ 1 - \left(\frac{350}{14}\right)^{0.3/2.6} \right] \\ &= 24,500,000(1 - 1.45) = -11,000,000 \text{ ft-lb/min, or } 333 \text{ hp} \end{aligned}$$

For two-stage compression, the saving is  $410 - 333 = 77$  hp, or about 19 per cent.

**9:11. Clearance Factor and Volumetric Efficiency.** Equations (9:49) to (9:51) state the theoretical work required for the compression of 1 lb of a gas in a cylinder without clearance. The introduction of clearance, necessary in the reciprocating compressor, will not increase the theoretical work of compression per pound of gas cleared through the discharge valve since that portion of the charge which is trapped in the clearance space

requires work during compression but restores an equal amount during its eventual expansion to suction pressure. The effect of clearance is to increase the necessary piston displacement for a given capacity and therefore to increase somewhat the work required by the actual compressor, due to its irreversibilities.

In Figure 9:9 is shown a theoretical indicator diagram of an ideal compressor with clearance.  $V_3$  is the clearance volume,  $V_1 - V_3$  is the piston displacement, and it is assumed that the value of  $n$  during expansion of the

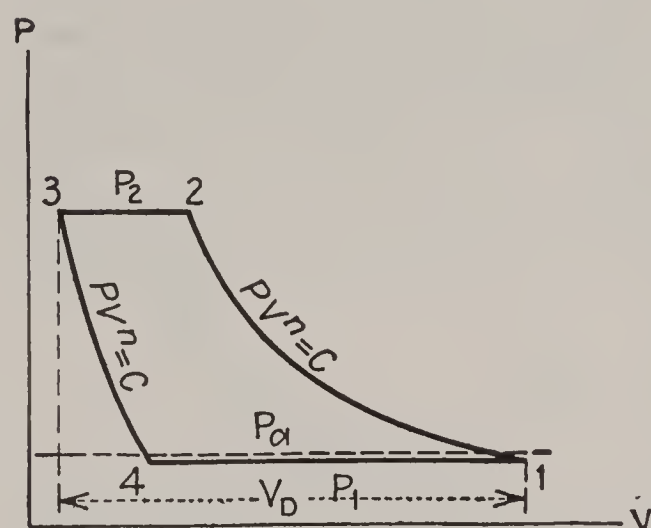


FIG. 9:9. Effect of clearance on compression.

gas trapped in the clearance space is the same as during the compression from  $V_1$  to  $V_2$ . At point 4 the intake valve opens in response to lowered pressure within the cylinder, and the fresh charge mixes with the gas that was trapped in the clearance space. The assumption that  $n$  is the same for expansion 3-4 as for compression 1-2 is necessary if irreversibility is to be avoided during the process 4-1 due to the mixing of bodies of gas at different temperatures.<sup>1</sup>

The clearance is usually expressed, in terms of the piston displacement, as  $V_3 = CV_D$ , in which  $V_D$  represents the piston displacement and is equal to  $V_1 - V_3$ . The quotient  $(V_1 - V_4)/V_D$  measures the ratio of the volume of the fresh charge drawn into the cylinder per cycle, *measured at suction pressure  $P_1$* , to the piston displacement of the compressor and is called the *clearance factor*. It may be calculated in terms of the clearance, as follows:

$$\begin{aligned}
 V_1 &= V_D + CV_D & P_3V_3^n &= P_4V_4^n \text{ or } V_4 = V_3 \left( \frac{P_3}{P_4} \right)^{1/n} = CV_D \left( \frac{P_2}{P_1} \right)^{1/n} \\
 \text{Clearance factor} &= \frac{V_1 - V_4}{V_D} = \frac{1}{V_D} \left[ V_D + CV_D - CV_D \left( \frac{P_2}{P_1} \right)^{1/n} \right] \\
 &= 1 + C - C \left( \frac{P_2}{P_1} \right)^{1/n} \tag{9:54}
 \end{aligned}$$

<sup>1</sup> Since, in the actual compressor, the temperature of the cooling fluid in the jacket continues to remain below that of the gas within the cylinder for the expansion 3-4 as for the compression 1-2, the heat flow may be expected to remain negative, *i.e.*, from the gas to the jacket, over at least much of the expansion. This would correspond to a value of  $n$  greater than  $k$  for the actual expansion of the trapped portion of the charge, instead of less than  $k$  as for the compression 1-2. Another somewhat unrealistic feature of the assumption is that the temperatures at 3 and 2 are assumed equal, and thus no cooling of the charge is assumed to take place during its delivery.



The term *free air* refers to the volume of air handled by an air compressor as measured at atmospheric pressure and temperature. This volume is less than as measured at suction pressure because of the differential of pressure,  $P_a - P_1$ , necessary to maintain flow from the atmosphere into the cylinder during the suction stroke. The ratio of the volume of the fresh charge of air drawn into the cylinder per cycle, *measured at atmospheric pressure*  $P_a$  (on the free-air basis), to the piston displacement is called the *volumetric efficiency*. The volumetric efficiency is a ratio slightly smaller than the clearance factor. In order to find its value, it is necessary to calculate the free-air volume as a proportion of the volume when measured at suction pressure. It has been shown in Art. 9:9 that  $T_1 = T_a$ . Therefore  $P_a V_a = P_1 V_1$  and  $V_a/V_1 = P_1/P_a$ . Thus, if the volume drawn into the cylinder per cycle, as measured at suction pressure (the clearance factor), is multiplied by the ratio  $P_1/P_a$ , the result will be the equivalent free-air volume, or

$$\eta_v = \frac{P_1}{P_a} \frac{V_1 - V_4}{V_D} = \frac{P_1}{P_a} \left[ 1 + C - C \left( \frac{P_2}{P_1} \right)^{1/n} \right] \quad (9:55)$$

in which  $\eta_v$  = volumetric efficiency, a decimal fraction

$P_1$  = suction pressure (within cylinder)

$P_a$  = pressure of atmosphere

An analysis of Eqs. (9:54) and (9:55) will indicate that both the clearance factor and the volumetric efficiency will decrease with increasing clearances and increasing pressure ratios of compression.

Compressors are often rated on the basis of their capacity in cubic feet of free air per minute. If the volume of free air to be handled per stroke is divided by the volumetric efficiency, the result will be the necessary displacement volume of the compressor. It will also be noted that  $P_a V_a$  may be substituted for  $P_1 V_1$  in Eqs. (9:49) to (9:51) for the calculation of the theoretical work per pound of air compressed.

*Example 9:11.* A two-stage double-acting air compressor, operating at 120 rpm, is to compress 200 ft<sup>3</sup> of free air per minute from 14 to 350 psia. The clearance at both ends of both cylinders may be assumed to be 3 per cent and the value of  $n$  during compression as 1.3. Atmospheric pressure is 14.7 psia. Calculate (a) the optimum pressure at discharge from the low-pressure stage, (b) the theoretical horsepower required for each stage and for the total compression, and (c) the necessary piston displacements of the low- and the high-pressure cylinders.

*Solution:*

$$(a) \quad \frac{P_i}{P_1} = \left( \frac{P_2}{P_1} \right)^{1/X} = \left( \frac{350}{14} \right)^{\frac{1}{2}} = 5 \quad \text{or} \quad P_i = (14)(5) = 70 \text{ psia}$$

$$\begin{aligned} (b) \quad W_{\text{low-pressure cylinder per min}} &= \frac{n}{n-1} P_a V_a \left[ 1 - \left( \frac{P_i}{P_1} \right)^{(n-1)/n} \right] \\ &= \left( \frac{1.3}{0.3} \right) (14.7)(144)(200) \left[ 1 - \left( \frac{70}{14} \right)^{0.3/1.3} \right] \\ &= 1,835,000(1 - 1.45) = -825,000 \text{ ft-lb/min, or 25 hp} \end{aligned}$$

The same horsepower will be required for the high-pressure stage, making a total of 50 hp. This calculation takes no account of a drop in pressure between the two cylinders; we shall assume this to be 1 psi. As an approximation, this difference of pressure will be divided equally between the two cylinders, making the discharge pressure from the first stage 70.5 psia, the suction pressure for the high-pressure cylinder 69.5 psia. Making these corrections,

$$W_{\text{low-pressure cylinder per min}} = 1,835,000 \left[ 1 - \left( \frac{70.5}{14} \right)^{0.231} \right] \\ = -830,000 \text{ ft-lb/min, or 25.1 hp}$$

A check of the power required by the high-pressure cylinder will show about the same value. This gives a total of 50.2 hp which may be considered to differ negligibly from the 50 hp calculated above since both these values must be adjusted upward to provide for the irreversibilities of the real compressor.

(c) For the low-pressure cylinder, the volumetric efficiency is, from Eq. (9:55),

$$\eta_v = \left( \frac{14}{14.7} \right) \left[ 1 + 0.03 - 0.03 \left( \frac{70.5}{14} \right)^{1/1.3} \right] = 0.952[1.03 - (0.03)(3.46)] = 0.882$$

The displacement volume may be calculated by dividing the volume of free air per minute by the volumetric efficiency and the number of charges compressed per minute,

$$V_{D\text{low-pressure cylinder}} = \frac{200}{(0.882)(2)(120)} = 0.945 \text{ ft}^3$$

Allowing for the piston rod, this volume corresponds to a bore and stroke of approximately 12 and 15 in., respectively.

For the high-pressure cylinder,

$$\eta_v = \left( \frac{69.5}{70.5} \right) \left[ 1 + 0.03 - 0.03 \left( \frac{350}{69.5} \right)^{1/1.3} \right] = 0.918$$

When the air has been cooled to atmospheric temperature in the intercooler after discharge from the low-pressure cylinder, the volume per minute is

$$V_i = \frac{P_a V_a}{P_i} = \frac{(14.7)(200)}{70.5} = 41.6 \text{ cfm}$$

and the piston displacement of the high-pressure cylinder,

$$V_{D\text{high-pressure cylinder}} = \frac{41.6}{(0.918)(2)(120)} = 0.189 \text{ ft}^3$$

Assuming that the stroke is the same as that of the low-pressure cylinder (15 in.), this displacement volume corresponds to a bore of about 5.25 in.

**9:12. Steady-flow Expansion of Gases.** In Fig. 9:5, it is indicated that the air leaving the compressor is to be the supply for an air engine. The development of power from compressed air is not, of course, its only use, but compressed air has certain advantages as a source of power since it may be transmitted over relatively long distances without excessive loss of energy.

The steady-flow expansion of a gas may be carried out in an engine or a turbine; in either case the maximum work obtainable from the expansion is the same. A review of Art. 9:8 indicates that Eqs. (9:49) to (9:51) are just as suitable for application to the expansion of gases as to their com-



pression. For the expansion, the initial state is at the higher pressure, and  $P_2/P_1$  is less than unity. Examination of the equations shows that this will be reflected in a change of the sign of the work. Except for this difference in sign, when steady-flow compression and expansion take place reversibly between the same limiting pressures and volumes, the work of expansion should equal the work of compression if  $n$  has the same value for both processes.

*Example 9:12.* Assume the air discharged from the adiabatic compression of Example 9:9 to enter and expand to 14 psia in a reversible adiabatic turbine. What horsepower is delivered by the turbine?

*Solution.* At exit from the compressor (and entrance to the turbine), the temperature of the air is  $530(\frac{3.5}{1.4})^{0.4/1.4} = 1330^\circ\text{R}$ . Applying Eq. (9:49) to the expansion in the turbine:

$$\begin{aligned} W \text{ per min} &= \frac{k}{k-1} MRT_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \\ &= \left( \frac{1.4}{0.4} \right) (100)(144)(1330) \left[ 1 - \left( \frac{14}{350} \right)^{0.286} \right] \\ &= 24,850,000(1 - 0.398) = +14,950,000 \text{ ft-lb/min, or } 453 \text{ hp} \end{aligned}$$

This is the same as the horsepower required for reversible adiabatic compression.

When a reciprocating engine is used to deliver power as the result of the expansion of compressed air, the valves must be operated mechanically rather than in response to pressure differentials. The volume of the compressed-air charge admitted to the cylinder per cycle is thus adjusted independently of the pressure ratio of expansion, and the pressure reached by the charge at the end of the power stroke of the piston is usually above the final exhaust pressure (the pressure of the atmosphere). The theoretical indicator diagram of the air engine will then show a vertical drop in pressure from this pressure to atmospheric pressure as the exhaust valve opens at the end of the power stroke; this represents a process during which the first portion of the charge to escape from the cylinder is (irreversibly) throttled to atmospheric pressure as the valve opens. Exhaust then proceeds at atmospheric pressure until the exhaust valve is mechanically closed.

Although the power output of a given engine can be increased by admitting a greater volume of air per cycle, the amount of work realized *per unit volume of compressed air supplied* is less than if the adiabatic expansion is completed to atmospheric pressure. The cycle of the reciprocating engine and the effect of engine clearance are discussed in greater detail in Chap. 13, though with particular reference to a more important type of reciprocating engine, the steam engine.

### Problems

*In the following list of problems, the specific heats of a perfect gas will be assumed constant unless the problem states otherwise.*

1. Show that what has been called an ideal gas in earlier chapters is recognizable as a perfect gas. What relation exists between  $C$  and  $R$ ?
2. Identify each of the ideal gases  $W$ ,  $X$ ,  $Y$ , and  $Z$  with a perfect gas listed in Table 9:1.
3. Describe the surface represented by the primary equation of state of a perfect gas. What is the trace of this surface on the plane  $T = 0$ ? On the plane  $T = 100$ ? On the plane  $T = 500$ ? What effect on the surface results from an increase in the gas constant?
4. Using absolute temperatures as ordinates and absolute pressures as abscissas, prepare a chart showing the variation of pressure and temperature of a perfect-gas system during changes of state which take place at constant volume. What is the pressure of the system at  $T = 0$ ? Interpret in terms of molecular activity.
5. A new temperature scale is devised. The volume of a perfect-gas system at  $0^\circ$  on this scale and a pressure of 20 psia is 11 ft<sup>3</sup>. At the same pressure, but a temperature of 100 deg on this temperature scale, the volume of the system is 14 ft<sup>3</sup>. Locate absolute zero on this temperature scale.
6. A perfect-gas system is confined in a closed rigid tank under a pressure of 50 psia. Its temperature, as measured on a certain temperature scale, is 170 deg. The pressure decreases as heat is withdrawn from the system until it becomes 30 psia; the corresponding temperature is  $-20$  deg. At what temperature is absolute zero located on this temperature scale?
7. What is the volume of 3 lb of oxygen at a vacuum of 5 in. Hg and a temperature of  $60^\circ\text{F}$ ? Barometer = 14.7 psia.
8. A tank contains 3 lb of air at a temperature of  $100^\circ\text{F}$ . The internal volume of the tank is 8 ft<sup>3</sup>. What pressure is recorded on a pressure gage attached to this tank? Barometric pressure is standard.
9. A certain perfect gas has a density of 0.068 lb/ft<sup>3</sup> at so-called "standard conditions" ( $p = 14.7$  psia,  $t = 32^\circ\text{F}$ ). What is the value of its gas constant?
10. At a pressure of 75 psia, 3 lb of nitrogen has a volume of 7 ft<sup>3</sup>. What is its temperature?
11. As a certain perfect-gas system weighing 3 lb increases in temperature from 100 to  $210^\circ\text{F}$  during a reversible constant-pressure process, 15,000 ft-lb of work is performed. What is the molecular weight of the gas?
12. A certain perfect gas has a molecular weight of 60. How much work would result from a reversible constant-pressure process during which 5 lb of this gas decreased  $10^\circ\text{F}$  in temperature?
13. Chlorine (Cl) has an atomic weight of 35.5. What is the gas constant for methyl chloride (CH<sub>3</sub>Cl) in the pressure-temperature range in which it acts as a perfect gas?
14. At atmospheric pressure and temperature, nitric oxide (NO) may be treated as a perfect gas. What is its density at standard atmospheric pressure and  $70^\circ\text{F}$ ?
15. The monatomic gas argon has an atomic weight of 39.9. Calculate its density at standard atmospheric pressure and  $70^\circ\text{F}$ .
16. A tank with a volume of 10 ft<sup>3</sup> contains air at 400 psia and  $70^\circ\text{F}$ . A second tank having a volume of 1 ft<sup>3</sup> contains air at 14.7 psia and  $70^\circ\text{F}$ . The two tanks are connected, and the pressure is allowed to equalize. What is the final pressure if the final temperature is  $70^\circ\text{F}$ ? What weight of air has been exchanged?
17. An observation balloon weighs 750 lb, including its load but not its gas contents. The balloon is filled with helium until it just floats in air at standard atmospheric pressure and a temperature of  $70^\circ\text{F}$ . What weight of helium is required? What volume? Assume equilibrium with the atmosphere.
18. One-tenth mole of a perfect gas is confined within a tank at 14.7 psia and  $32^\circ\text{F}$ . What is the internal volume of the tank?



19. A tank contains 2.016 lb of hydrogen at 100 psia and 70°F. Sixteen pounds of oxygen is forced into the tank. If the temperature of the mixture is 70°F, what is the total pressure of the mixture? What are the partial pressures of the hydrogen and the oxygen?

20. As the result of a negligible spark, the mixture of Prob. 19 burns completely to  $\text{H}_2\text{O}$ . Assuming the products of the combustion to be a perfect gas, what would be the pressure within the tank when the original temperature is again reached? What weight of  $\text{H}_2\text{O}$  is formed? What volume? According to the steam tables, are these values consistent? State your conclusions as to what must have happened to the water vapor. On this new basis, what is the pressure within the tank? What does the tank contain?

21. A tank contains 12 lb of solid carbon having a negligible volume and 32 lb of oxygen at a pressure of 14.7 psia and 70°F. A negligible spark ignites the carbon, and it burns completely to  $\text{CO}_2$ . After the products of combustion have returned to a temperature of 70°F, what is the pressure within the tank?

22. Air is a mixture of approximately 23.5 parts by weight of oxygen and 76.5 parts of nitrogen. In air having a total pressure of 14.7 psia, what are the partial pressures of the oxygen and the nitrogen? Calculate the "apparent" gas constant for air on the basis of the composition as stated.

23. Five pounds of air increases in temperature from 60 to 140°F. During the process neither the pressure nor the volume is constant. What is the change of internal energy of the system?

24. Two pounds of air undergoes a process during which the heat flow is +50 Btu and 10,000 ft-lb of work is performed by the system. What is the change of temperature of the air?

25. An air system weighing 1 lb has a pressure of 50 psia and a volume of 4 ft<sup>3</sup>. As the result of a certain process, its pressure changes to 70 psia and its volume to 3.2 ft<sup>3</sup>. What is the change of internal energy of the system? What is its change of enthalpy? Repeat solution, but based on a weight of 1.5 lb. Compare your answers as based on the two system weights. Develop an equation expressing the change of internal energy of a perfect-gas system in terms of the gas constant, the ratio  $k$ , and the initial and final pressures and total volumes of the system, assuming the specific heats to be constant. Write a similar expression for the change of enthalpy.

26. The ratio  $k$  for methyl chloride (see Prob. 13) is 1.2. What are the changes of specific internal energy and specific enthalpy when the temperature decreases by 30°F?

27. Write an expression for the change of internal energy of a perfect-gas system in terms of its weight, its gas constant, the ratio of the specific heats, and the initial and final absolute temperatures. Write a similar expression for the change of enthalpy.

28. Can the specific heats  $c_v$  and  $c_p$  of a perfect gas increase with temperature? If they do increase, does the difference between them necessarily remain constant? To what effect would you attribute the increase? Can  $c_v$  and  $c_p$  decrease with temperature?

29. Calculate the values of  $c_v$  and  $c_p$  for argon (see Prob. 15) at atmospheric levels of temperature. As a perfect gas, what are the maximum values of  $c_v$  and  $c_p$  which are possible for argon?

30. Calculate the values of  $c_v$  and  $c_p$  for nitric oxide (NO) at atmospheric temperature. As a perfect gas, what maximum values of  $c_v$  and  $c_p$  are conceivable for this gas?

31. As the result of a reversible polytropic process, the pressure of an air system changes from 200 to 20 psia while its volume increases from 1 to 9 ft<sup>3</sup>. What is the value of  $n$ ? What is the external work? What is the change of internal energy? The heat flow? The change of enthalpy?

32. The pressure of a 1-lb air system increases from 14.7 to 50 psia, its temperature from 60 to 230°F, during a reversible polytropic process. What is the value of  $n$ ? What is the external work? What is the change of internal energy? The heat flow? The change of enthalpy?

33. A closed system consists of 1 lb of air. Its initial pressure is 30 psia, and its initial volume is 7 ft<sup>3</sup>. If, during each of the following processes, its volume increases to 10 ft<sup>3</sup>, find the heat flow, the change of internal energy, the change of enthalpy, and the external work in each case: (a) reversible constant pressure; (b) reversible constant temperature; (c) reversible adiabatic; (d) adiabatic expansion into an exhausted space; (e) reversible with  $n = -1$ ; (f) reversible constant internal energy; (g) reversible constant enthalpy.

34. During the reversible polytropic compression of a perfect-gas system, the temperature rises and heat enters the system. Is the value of  $n$  between 0 and 1, between 1 and  $k$ , between  $k$  and  $\infty$ , or does  $n$  have a negative value?

35. During the reversible polytropic compression of an air system, the heat flow is out of the system and is equal to one-third of the external work. What is the value of  $n$ ?

36. One pound of air has an initial pressure of 100 psia and an initial volume of 2.5 ft<sup>3</sup>. At the end of a reversible process that is represented by a straight line on a  $Pv$  diagram, the pressure is 20 psia, and the volume 9 ft<sup>3</sup>. What is the change of internal energy during the process? What is the heat flow? Between what values does the polytropic specific heat  $c_n$  vary during the process?

37. During an irreversible process which follows the state path  $Pv^n = \text{const}$ , with  $n$  constant, the pressure of an air system changes from 120 to 30 psia and its volume from 2 to 6 ft<sup>3</sup>. During the process the specific heat is constant, and the total heat flow for the process is  $-10$  Btu. What is the value of  $n$ ? What fraction of the maximum work possible in following the same state path is lost because of the irreversibility of the process?

38. Calculate the change of entropy of the system in Probs. 25, 32, 33(a) to (g), and 36.

39. A Carnot engine uses air as the working substance, operating between source and refrigerator temperatures of 500 and 60°F, respectively. The pressure and volume at the beginning of the isothermal expansion are 300 psia and 4 ft<sup>3</sup>. During the isothermal expansion, the change of entropy is 0.16. Determine the pressures and volumes at the end of each process of the cycle. Calculate the work of each process and the net work of the cycle. Calculate the heat flow from the source, the heat rejected to the refrigerator, and the net heat flow of the cycle. What is the efficiency of the cycle?

40. What horsepower is theoretically required for the isothermal compression of 1000 ft<sup>3</sup> of air per minute from 14.5 to 50 psia in a single-stage compressor? What horsepower if the compression is adiabatic? If  $n = 1.3$ ?

41. Compare the horsepower necessary to compress 800 cfm from 14.7 to 45 psia in a single-stage compressor for oxygen and for nitrogen. Assume  $n$  is the same during the compression of both gases. What are the relative weights which are compressed per minute if the temperature at the beginning of compression is the same?

42. What horsepower is theoretically required for the compression of 30 lb of air per minute from 14 to 900 psia in a single-stage compressor, if  $n = 1.32$ ? Atmospheric temperature is 70°F.

43. A centrifugal fan handles 5000 ft<sup>3</sup> of air per minute against a total head of 5 in. of water. Calculate the theoretical fan horsepower.

44. The total head against which a fan operates is the sum of the static (pressure) head and the velocity head (the difference of the kinetic energies per pound at intake



to and discharge from the fan, expressed in terms of the distance through which this energy would lift a unit weight). A propeller type of fan handles 25,000 ft<sup>3</sup> of air at 14.7 psia and 70°F per minute, increasing it from negligible velocity to a velocity of 25 mph. The static pressures at intake to and discharge from this fan, at the points where the velocities are measured, are balanced. Calculate the theoretical fan horsepower.

45. Calculate the horsepower theoretically required as based on the data of Prob. 42 if three stages of compression are used. What are the pressures at discharge from each stage?

46. Prove that if  $G$  (see Art. 9:10) is to have a minimum value then  $P_i^2 = P_1 P_2$ .

47. What horsepower is theoretically required for the compression of 1000 ft<sup>3</sup> of air per minute from 14 to 200 psia with  $n = 1.3$  if two stages of compression are used? What is the pressure at discharge from each stage? What is the saving over single-stage compression?

48. A compressor with 3 per cent clearance operates at a suction pressure of 14.2 psia when atmospheric pressure is 14.7 psia. The discharge pressure is 60 psia, and  $n = 1.32$ . What is the clearance factor? The volumetric efficiency? If this compressor handles 1400 ft<sup>3</sup> of free air per minute, is double-acting, and operates at 150 rpm, what is its piston displacement?

49. The total cylinder volume of a double-acting compressor with equal clearances at the two ends of the cylinder is 5.3 ft<sup>3</sup>. Its piston displacement is 5 ft<sup>3</sup>, and it makes 80 rpm. The suction pressure is 14.3 psia, discharge pressure is 45 psia, atmospheric pressure is standard, and  $n = 1.3$  for the compression. What is its capacity in cubic feet of free air per minute? What is its theoretical horsepower?

50. One hundred cubic feet of air at 150 psia and 600°F is supplied per minute to a reversible adiabatic engine which exhausts at 14.7 psia. What horsepower does the engine deliver? What is the temperature of its exhaust?

51. If air at the state and at the rate described in Prob. 50 is delivered to an engine which has a cylinder surrounded by a water jacket containing water at 70°F, would you expect to find the value of  $n$  increased or decreased in comparison with its value for the adiabatic engine? Would the power output of the engine have been increased or decreased? Assuming that lubrication difficulties could be overcome without water-jacketing, would you consider it desirable to water-jacket an engine cylinder?

### Symbols

$c_n$	polytropic specific heat, general
$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$C$	a constant; also, ratio of clearance volume to piston displacement
$f$	impact force of a molecule
$F$	impact force of a collection of molecules
$h$	enthalpy of unit mass
$H$	enthalpy of a system
$J$	proportionality factor
$k$	ratio of the specific heats
$m$	molecular weight; mass of a molecule
$M$	mass of a system; mass rate of flow
$n$	a constant
$N$	number of molecules in a system of unit volume
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	heat flow; rate of heat flow

$R$	gas constant
$s$	entropy of unit mass
$S$	entropy of a system
$T$	absolute temperature
$u$	internal energy of unit mass
$U$	internal energy of a system
$v$	specific volume
$V$	volume of a system; also, volume rate of flow
$V_D$	piston displacement volume
$\bar{V}$	velocity
$W$	work; rate of work delivery
$X$	number of stages of compression
$z$	elevation

*Greek Letters*

$\eta_v$	volumetric efficiency
$\mu$	Joule coefficient
$\mu_J$	Joule-Thomson coefficient
$\rho$	mass density

*Subscripts*

$a$	atmospheric; free-air basis
$i$	intermediate
$m$	molar; of a mole
$n$	polytropic (see $c_n$ )
$p$	constant pressure
rev	reversible
$T$	constant temperature
$u$	constant internal energy
$v$	constant volume



## CHAPTER 10

### MIXTURES OF GASES AND VAPORS

#### MIXTURES OF PERFECT GASES

**10:1. Basic Principles.** The engineer often deals with mixtures of gases, and it is necessary to develop methods by which the properties of such mixtures may be determined. Although air is perhaps the outstanding example of these mixtures, many others may be cited, including air-fuel mixtures and the products of combustion. When the pressures of the various constituents are uniformly low as compared with their critical pressures and when they remain in the gaseous phase throughout the engineering process, they may be treated as perfect gases with the accuracy usually sufficient for the engineering calculation. It has been indicated in Chap. 9 that the thermodynamic method of handling these mixtures consists in finding an average molecular weight (the weight of 1 mole) of the mixture and thereafter treating the mixture as if it were composed of a single gas having molecules of a relative weight equal to this average; the mixture thus becomes, in effect, a new "pure substance."

According to the principle first stated by Dalton, any gas, in a mixture of gases, acts as if it were in a vacuum and the other gases were not present. The basis of this principle, as it applies to the perfect gas, was outlined in Art. 9:2. Gibbs restated the Dalton principle in the more specific and usable form which we know as the *Gibbs-Dalton law*:

*The pressure, internal energy, and entropy of a mixture of gases are, respectively, equal to the sums of the pressures, internal energies, and entropies of the component gases when each occupies alone the volume of the mixture at the temperature of the mixture.*

Although the Gibbs-Dalton law is based on the concept of the perfect gas, experience has shown that it holds for real gases with close accuracy, especially at low pressures.

Let us consider a simple system consisting of a mixture of a number of gases which we shall designate as 1, 2, 3, etc. These gases occupy a common volume, the volume of the mixture, and we may accordingly write

$$V_1 = V_2 = V_3 = \cdots = V_n = V_m \quad (10:1)$$

in which the subscripts 1 to  $n$  refer to the component gases and  $m$  to the mixture. Assuming the mixture to be in equilibrium, the temperature of

all components must also be the same and equal to the temperature of the mixture, or

$$T_1 = T_2 = T_3 = \dots = T_n = T_m \quad (10:2)$$

According to the Gibbs-Dalton law,

$$P_1 + P_2 + P_3 + \dots + P_n = P_m \quad (10:3)$$

in which  $P_1$  to  $P_n$  are the *partial pressures* created by the bombardment of the molecules of the respective gases and  $P_m$  is their sum, the *total pressure* of the mixture. Further, from the same law,

$$U_1 + U_2 + U_3 + \dots + U_n = U_m \quad (10:4)$$

and

$$S_1 + S_2 + S_3 + \dots + S_n = S_m \quad (10:5)$$

Also,  $H_1 = U_1 + P_1 V_1/J = U_1 + P_1 V_m/J$ ,  $H_2 = U_2 + P_2 V_m/J$ , etc., and since the sum of the internal energies of the components is  $U_m$  and the sum of their partial pressures is  $P_m$ ,

$$H_1 + H_2 + H_3 + \dots + H_n = U_m + \frac{P_m V_m}{J} = H_m \quad (10:6)$$

Finally, the mass of the mixture is equal to the sum of the masses of its components,  
or

$$M_1 + M_2 + M_3 + \dots + M_n = M_m \quad (10:7)$$

The relations expressed by Eqs. (10:1) to (10:7) are the foundation underlying the calculation of the properties of the mixture.

**10:2. Definitions.** A mole of any gas (or, indeed, of any liquid or solid) consists of a standard number of molecules (see Art. 9:2). This is true whether the gas is composed of molecules which all have the same mass or whether, as in a mixture, it is a collection of molecules of different mass. If the mixture is composed of perfect gases, the volume of the mole will be the same at the same pressure and temperature for any mixture as for the component gases, considered individually. This characteristic of the mole makes it a convenient unit on which to base definitions of mixture composition and calculations of mixture properties.

In describing the composition of a mixture of gases, various methods may be used. For instance, the amounts of the various components may be stated in terms of their *mole fractions*. *The mole fraction of a component gas in a mixture of gases is the ratio of the number of moles of that gas in a given volume of the mixture to the total moles of the mixture in that volume.* The analysis of a mixture to obtain the mole fractions of its component gases can be readily made, for, at the same pressure and temperature, equal volumes of all perfect gases (or mixtures of perfect gases) contain



the same number of molecules and therefore the same number of moles. In practice, these analyses are made by means such as the Orsat analyzer. The method used is to separate a sample of the mixture and measure its volume at atmospheric pressure and temperature. One of the component gases is then chemically absorbed from the mixture, and the remaining volume is measured at the same pressure and temperature; the difference between this and the original volume measures the amount of that component in the mixture, the ratio of the difference to the original volume of the mixture being the mole fraction  $x_1$  assigned to that component. The next component is then absorbed from the remainder of the sample, and  $x_2$ , its mole fraction, is obtained by comparing the decrease in volume due to its removal with the original volume of the mixture sample. This is continued until account is taken of all components of the mixture.

The result of an Orsat analysis is often called the *volumetric analysis*, or *proportion by volume*, but corresponds to a description of the mixture in terms of its mole fractions. Because each of the component gases actually occupies the full volume of the mixture, the use of "mole fraction" is to be preferred to "proportion by volume."

Another method of describing gas mixtures is by means of the *gravimetric analysis*, or *proportion by weight*, of the various constituents. Referring to Eq. (10:7) and the notation used in that equation, the proportion by weight of component 1 is, for example,  $M_1/M_m$ .

**10:3. Calculation of Mixture Properties.** The state of a mixture of gases is usually defined in terms of its temperature  $T_m$  and its pressure  $P_m$ . The composition of the mixture may be presented either in terms of the mole fractions of its component gases (their proportions by volume) or, less frequently, in the form of a gravimetric analysis. Assuming that their mole fractions have been determined, the weights of the components in 1 mole of the mixture are, respectively,  $x_1m_1$ ,  $x_2m_2$ ,  $x_3m_3$ , etc., where  $m_1$ ,  $m_2$ ,  $m_3$ , etc., are the respective molecular weights (the weights of 1 mole) of the component gases. But

$$x_1m_1 + x_2m_2 + x_3m_3 + \cdots + x_nm_n = m_m \quad (10:8)$$

in which  $m_m$  is the weight of 1 mole of the mixture (the "apparent" molecular weight). When  $m_m$  has been obtained in this manner, the products  $x_1m_1$ ,  $x_2m_2$ ,  $x_3m_3$ , etc., may be compared with  $m_m$  to obtain the gravimetric analysis, as follows:

$$\frac{M_1}{M_m} = \frac{x_1m_1}{m_m} \quad \frac{M_2}{M_m} = \frac{x_2m_2}{m_m} \quad \text{etc.} \quad (10:9)$$

If, on the other hand, the composition of the mixture is described in terms of a gravimetric analysis, the corresponding division into mole fractions may be obtained since the proportion by weight from the gravi-

metric analysis is the weight of a component gas in 1 lb of the mixture and the division of this weight by the molecular weight of the component gas gives the number of moles of that gas in 1 lb of the mixture. The sum of these quotients for all of the components is therefore the number of moles of the mixture in 1 lb of the mixture, or  $1/m_m$ . Thus,

$$\frac{M_1}{M_m} \frac{1}{m_1} + \frac{M_2}{M_m} \frac{1}{m_2} + \frac{M_3}{M_m} \frac{1}{m_3} + \cdots + \frac{M_n}{M_m} \frac{1}{m_n} = \frac{1}{m_m} \quad (10:10)$$

from which  $m_m$  may be calculated. Then, from Eq. (10:9),

$$x_1 = \frac{M_1}{M_m} \frac{m_m}{m_1} \quad x_2 = \frac{M_2}{M_m} \frac{m_m}{m_2} \quad \text{etc.} \quad (10:11)$$

It has been shown above how  $m_m$ , the weight of 1 mole of the mixture, may be obtained from the proportions of the mixture, whether those proportions be expressed in terms of mole fractions or in the form of a gravimetric analysis. Dividing this apparent molecular weight into the universal gas constant gives the value of  $R$ , the gas constant that applies to the mixture. Thereafter the equations of Chap. 9 will apply, exactly as if the mixture had been composed of a single kind of molecule. The values of  $c_p$  and  $c_v$  will, for the mixture, be the weighted average of their values for the component gases, as follows:

$$c_{p_m} = \frac{M_1}{M_m} c_{p_1} + \frac{M_2}{M_m} c_{p_2} + \frac{M_3}{M_m} c_{p_3} + \cdots + \frac{M_n}{M_m} c_{p_n} \quad (10:12)$$

$$c_{v_m} = \frac{M_1}{M_m} c_{v_1} + \frac{M_2}{M_m} c_{v_2} + \frac{M_3}{M_m} c_{v_3} + \cdots + \frac{M_n}{M_m} c_{v_n} \quad (10:13)$$

According to the Dalton principle,  $P_1 V_1 = M_1 R_1 T_1$ ,  $P_2 V_2 = M_2 R_2 T_2$ , etc., and, substituting  $V_m$  for  $V_1$ ,  $V_2$ , etc.,  $T_m$  for  $T_1$ ,  $T_2$ , etc., and  $1545/m$  for  $R$ ,

$$P_1 V_m = \frac{1545 M_1 T_m}{m_1} \quad P_2 V_m = \frac{1545 M_2 T_m}{m_2} \quad \text{etc.}$$

Also  $P_m V_m = 1545 M_m T_m / m_m$ , and, dividing,

$$\frac{P_1}{P_m} = \frac{M_1}{M_m} \frac{m_m}{m_1} = x_1 \quad \frac{P_2}{P_m} = x_2 \quad \text{etc.} \quad (10:14)$$

$P_1$ ,  $P_2$ , etc., are the partial pressures of the component gases, and Eq. (10:14) shows that these can be obtained by multiplying the total pressure of the mixture by the respective mole fractions of its components.

*Example 10:3.* An Orsat analysis of the products of combustion resulting from the burning of a fuel gas yields the following percentages:  $\text{CO}_2$ —10;  $\text{O}_2$ —7;  $\text{N}_2$ —83. The water and water vapor have been removed from the sample before this analysis was made, and the analysis therefore presents the composition of the *dry* products. (a) Calculate the gravimetric analysis, the apparent molecular weight, and the gas constant



for the dry mixture. (b) Assuming the total pressure of the dry mixture to be 14.7 psia and the temperature 100°F, find the partial pressure of each component and the specific volume of the mixture. (c) Calculate the specific heats,  $c_p$  and  $c_v$ , of this dry mixture.

Solution:

(a) The Orsat analysis is a volumetric analysis, and the corresponding mole fractions are obtained by dividing the percentages by 100. The following tabular form of solution will be found convenient:

No.	Component	Mole fraction $x$	Mol. wt. $m$	Wt. per mole of mixture $xm$	Gravimetric analysis $M/M_m$
1	CO <sub>2</sub>	0.10	44	4.40	0.147
2	O <sub>2</sub>	0.07	32	2.24	0.075
3	N <sub>2</sub>	0.83	28.016	23.25	0.778
Total.....	...	....	.....	29.89	1.000

$$R_m = \frac{1545}{m_m} = \frac{1545}{29.89} = 51.7$$

(b)  $p_1 = x_1 p_m = (0.10)(14.7) = 1.47$  psia  
 $p_2 = x_2 p_m = (0.07)(14.7) = 1.03$  psia  
 $p_3 = x_3 p_m = (0.83)(14.7) = 12.20$  psia  
14.7 psia

$$v_m = \frac{R_m T_m}{P_m} = \frac{(51.7)(560)}{(14.7)(144)} = 13.65$$
 ft<sup>3</sup>/lb

(c) The specific heats of the component gases may be taken from Table 9:1. Then

$$c_{p_m} = (0.147)(0.201) + (0.075)(0.217) + (0.778)(0.248) = 0.239$$
$$c_{v_m} = (0.147)(0.156) + (0.075)(0.155) + (0.778)(0.177) = 0.172$$

The specific heats of air are often used to apply to the dry products of combustion in approximate calculations. A comparison of the values calculated above with the corresponding values for air indicates why this is possible. Although the dry products vary somewhat in composition as various fuels are burned with different weights of air supply per pound of fuel, the variation of  $c_p$  and  $c_v$ , within the usual limits of composition, is minor.

**10:4. Adiabatic Mixing Processes for Perfect Gases.** To aid our study of the nonflow mixing process, let us refer to Fig. 10:1, which shows a rigid insulated container that has been divided into a number of compartments (three are shown in the figure, but the number need not be limited) by rigid insulated partitions which are removable and occupy a negligible portion of the total volume of the vessel. Originally, gas 1 is confined in compartment  $a$  at pressure  $P_a$  and temperature  $T_a$ , gas 2 in compartment  $b$  at  $P_b$  and  $T_b$ , etc.

For the first example, we shall assume that the individual pressures and temperatures of all these gases are the same. If the partitions are now

removed, each gas will expand to occupy the total volume of the container. The resultant mixing process is adiabatic since heat flow is prevented by the insulation that covers the vessel walls; these walls are rigid, and no

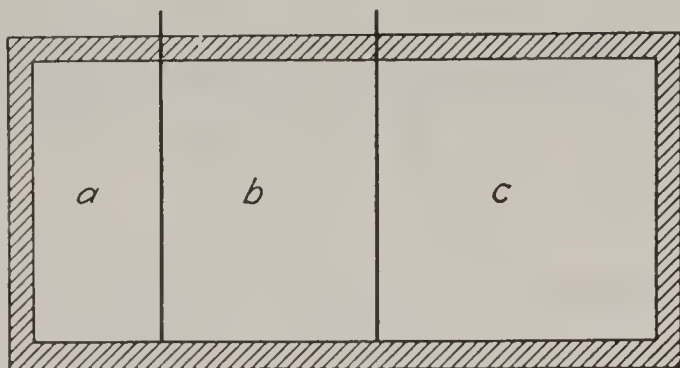


FIG. 10:1. Adiabatic nonflow mixing.

work is exchanged with any external system. Therefore the internal energy of the resulting mixture is the sum of the original internal energies of its parts before mixture took place. But these are perfect gases, and their internal energies are accordingly functions of their temperature alone and

independent of the volume they occupy. Therefore the temperature of the mixture must be identical with the original common temperature of its components.

Each gas has expanded at constant temperature, and Boyle's law will apply. Designating the original equal pressures  $P_a$ ,  $P_b$ , etc., as  $P$  and the partial pressures of the components in the final mixture as  $P_1$ ,  $P_2$ , etc., we may write

$$P_a V_a = P V_a = P_1 V_m \text{ or } \frac{P_1}{P} = \frac{V_a}{V_m} \quad P V_b = P_2 V_m \text{ or } \frac{P_2}{P} = \frac{V_b}{V_m}$$

But since the original pressures and temperatures were equal,  $V_a/V_m = x_1$ ,  $V_b/V_m = x_2$ , etc. Therefore  $P_1/P = x_1$ ,  $P_2/P = x_2$ , etc. From Eq. (10:14),  $P_1/P_m = x_1$ ,  $P_2/P_m = x_2$ , etc., and  $P_m$  must therefore equal  $P$ .

The mixing process has been adiabatic, but an analysis will indicate that it is irreversible, since external systems, not affected during the mixing process, must be called upon to supply energy if each of the component gases of the mixture is again to be restored to its individual compartment. We should therefore expect to find that the entropy had increased during mixing and was greater than the sum of the original entropies of the parts. Although the temperature of these parts has not changed during mixing, their pressures have individually decreased and their volumes have increased. A convenient choice may be made from Eqs. (9:44a) to (9:47a) for the calculation of the increase of entropy of each component; these individual increases may be added to obtain the total increase of entropy due to mixing.

Let us now consider a more complicated mixing process in which neither the pressures  $P_a$ ,  $P_b$ , etc., nor the temperatures  $T_a$ ,  $T_b$ , etc., are equal, though their magnitudes are individually known, as are the volumes  $V_a$ ,  $V_b$ , etc., and the kind of gas confined in each compartment. The weight



of gas in each compartment may be calculated and a gravimetric analysis of the mixture that will result when the partitions are removed thus obtained. Applying methods suggested in the preceding article, the gas constant of the mixture may be computed. The internal energy of the mixture is again the sum of the original internal energies of its parts, and though, in this case, each gas changes in internal energy, the sum of these changes must therefore be zero. Writing this relation in the form of an equation,

$$M_1c_{v1}(T_m - T_a) + M_2c_{v2}(T_m - T_b) + \cdots + M_nc_{vn}(T_m - T_n) = 0$$

(10:15)

in which  $T_m$ , the final temperature of the mixture, is the only unknown and therefore may be directly computed. This leaves  $P_m$  as the only unknown in the equation  $P_mV_m = M_mR_mT_m$  and makes its calculation possible. The increase of entropy for this adiabatic mixing process must not only account for the irreversibility of the mixing alone but also reflect the fact that the system was not originally in temperature and pressure equilibrium.

*Example 10:4.* The three compartments into which a closed insulated container is divided contain, respectively, 1 lb of hydrogen at 200 psia and 60°F, 1 lb of helium at 100 psia and 100°F, and 1 lb of carbon dioxide at 15 psia and 120°F. The partitions are removed, and a mixture is formed. (a) What are the mole fractions of each component in the mixture and the apparent molecular weight and gas constant of the mixture? (b) What is the temperature of the mixture? (c) Find the partial pressures of each component of the mixture. (d) Calculate the specific heats of the mixture and their ratio,  $k$ . (e) What change of entropy results from mixing?

*Solution:*

(a) A tabular form of solution is again convenient:

No.	Component	Gravimetric analysis $M/M_m$	Mol. wt. $m$	Moles per lb of mixture $M/M_m m$	Mole fraction $Mm_m/M_m m$
1	H <sub>2</sub>	0.333	2.016	0.1655	0.645
2	He	0.333	4.002	0.0833	0.325
3	CO <sub>2</sub>	0.333	44	0.0076	0.030
Total.....	...	.....	.....	0.2564	1.000

$$m_m = \frac{1}{0.2564} = 3.90; R_m = \frac{1545}{3.90} = 396$$

(b) Applying Eq. (10:15),

$$(1)(2.43)(t_m - 60) + (1)(0.755)(t_m - 100) + (1)(0.156)(t_m - 120) = 0$$

Solving,

$$t_m = 72^\circ\text{F}$$

$$(c) \quad V_m = V_a + V_b + V_c = \frac{M_a R_a T_a}{P_a} + \frac{M_b R_b T_b}{P_b} + \frac{M_c R_c T_c}{P_c}$$

$$= \frac{(1)(766.6)(520)}{(200)(144)} + \frac{(1)(386)(560)}{(100)(144)} + \frac{(1)(35.1)(580)}{(15)(144)} = 38.27 \text{ ft}^3$$

$$p_m = \frac{P_m}{144} = \frac{M_m R_m T_m}{144 V_m} = \frac{(3)(396)(532)}{(144)(38.27)} = 115 \text{ psia}$$

$$p_1 = x_1 p_m = (0.645)(115) = 74.0 \text{ psia}$$

$$p_2 = x_2 p_m = (0.325)(115) = 37.5 \text{ psia}$$

$$p_3 = x_3 p_m = (0.030)(115) = 3.5 \text{ psia}$$

$$\underline{115 \text{ psia}}$$

$$(d) \quad c_{p_m} = (0.333)(3.42) + (0.333)(1.25) + (0.333)(0.201) = 1.624$$

$$c_{v_m} = (0.333)(2.43) + (0.333)(0.755) + (0.333)(0.156) = 1.114$$

$$k_m = \frac{c_{p_m}}{c_{v_m}} = \frac{1.624}{1.114} = 1.46$$

(e) Applying Eq. (9:47a),

$$\Delta S_1 = M c_{p_1} \log_e \frac{T_m}{T_a} - \frac{M R_1}{J} \log_e \frac{P_1}{P_a} = (1)(3.42) \log_e \frac{532}{520} - \frac{(1)(766.6)}{778} \log_e \frac{74.0}{200}$$

$$= +0.078 + 0.978 \quad = +1.056$$

$$\Delta S_2 = (1)(1.25) \log_e \frac{532}{560} - \frac{(1)(386)}{778} \log_e \frac{37.5}{100} = -0.059 + 0.485 \quad = +0.426$$

$$\Delta S_3 = (1)(0.201) \log_e \frac{532}{580} - \frac{(1)(35.1)}{778} \log_e \frac{3.5}{15} = -0.017 + 0.066 \quad = +0.049$$

$$\Delta S = \underline{+1.531}$$

The foregoing analysis is concerned with the adiabatic *nonflow* mixing process. The mixing of streams of gases in steady flow is more charac-

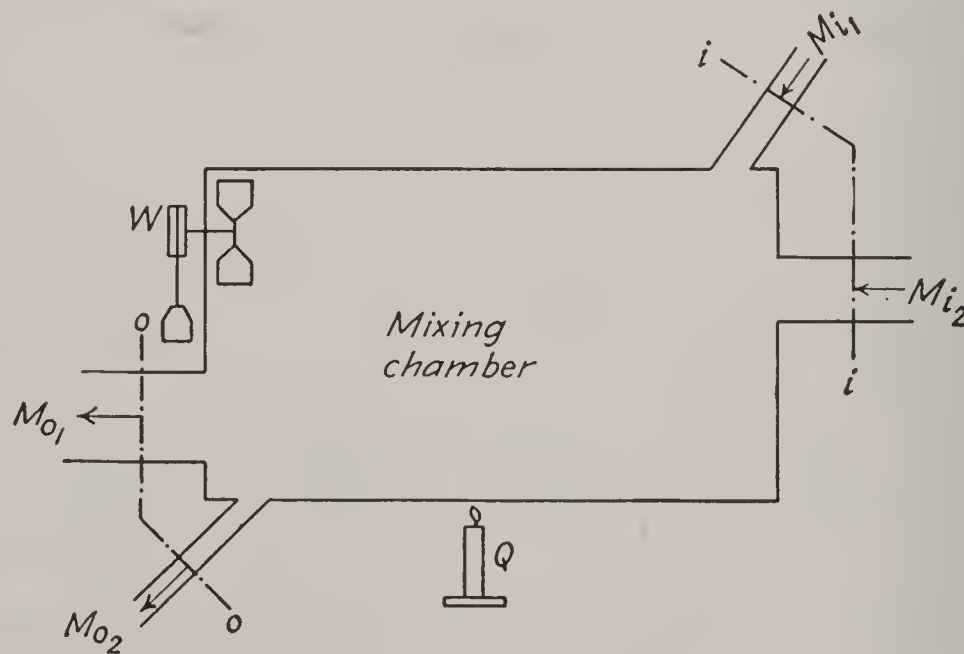


FIG. 10:2. Steady-flow mixing.

teristic of the usual engineering situation and is illustrated in Fig. 10:2. Section *i* is a section across all of the incoming streams of gas; section *o* intersects all outgoing streams. Applying the steady-flow energy equation [Eq. (3:5)], we may write



$$\sum_i M \left( h + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) + {}_iQ_o = \sum_o M \left( h + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) + {}_oW_o \quad (10:16)$$

in which  $\sum_i$  represents the summation for all incoming streams and  $\sum_o$  the corresponding summation for those leaving the mixing chamber.

If the mixing is adiabatic and no external work is performed, the  $Q$  and  $W$  terms in Eq. (10:16) will be zero. In addition, the difference between streams in stored energy due to motion and elevation will often be negligible in comparison with differences of enthalpy, and, for this set of circumstances, Eq. (10:16) simplifies to

$$\sum_i Mh = \sum_o Mh \quad (10:17)$$

It will be observed that the application of Eqs. (10:16) and (10:17) is not restricted to perfect gases but may be extended in application to the steady-flow mixing of any combination of fluids, including liquids.

**10:5. The isentropic process** for a mixture of gases having separately different values of  $k$ , the ratio of their specific heats, is of special interest. When, for example, the mixture is composed of a monatomic and a diatomic gas, the value of  $k$  for the mixture will be intermediate between 1.67 and 1.4. The isentropic for the mixture will follow the  $PV$  relation  $PV^k = C$ , where  $k$  has this intermediate value. But  $k_1 > k > k_2$ , where the subscript 1 refers to the monatomic and 2 to the diatomic component. In other words, although the process is isentropic for the mixture, it is not isentropic as regards the separate components. We may write

$$\Delta S_m = 0 = \Delta S_1 + \Delta S_2 \quad \text{or} \quad \Delta S_1 = -\Delta S_2 \quad (10:18)$$

$\Delta S_1$  and  $\Delta S_2$  may be calculated by applying the appropriate equation from Table 9:2, substituting  $k$  for  $n$  and  $k_1$  and  $k_2$ , successively, for  $k$  in the equation for the change of entropy during a polytropic process.

*Example 10:5.* The mixture of Example 10:4 expands isentropically to a final pressure of 20 psia. Find the individual entropy changes of its components.

*Solution.* For each component,  $n = k_m = 1.46$  for this expansion. The temperature at the end of the expansion is  $T_2 = T_1(P_2/P_1)^{n-1/n} = 532 \left(\frac{20}{115}\right)^{0.46/1.46} = (532)(0.55) = 293^\circ\text{R}$ . From Table 9:2,

$$\begin{aligned} \Delta S_{\text{H}_2} &= Mc_v \frac{n-k}{n-1} \log_e \frac{T_2}{T_1} = (1)(2.43) \left( \frac{1.46-1.41}{1.46-1} \right) \log_e 0.55 \\ &= (0.264)(-0.597) = -0.158 \\ \Delta S_{\text{H}_2\text{O}} &= (1)(0.755) \left( \frac{1.46-1.66}{1.46-1} \right) \log_e 0.55 = (-0.328)(-0.597) = +0.196 \\ \Delta S_{\text{CO}_2} &= (1)(0.156) \left( \frac{1.46-1.29}{1.46-1} \right) \log_e 0.55 = (0.058)(-0.597) = -0.035 \\ \Delta S_m &= +0.003 \end{aligned}$$

The discrepancy in  $\Delta S_m$  ( $\Delta S_m$  should total zero) is due to slide-rule error.

## MIXTURES OF A GAS AND A VAPOR

**10:6. Characteristics of Gas-vapor Mixtures.** According to the distinction that has been made between the meanings of the terms gas and vapor, as we shall use them (see Art. 9:1), the vapor component of a gas-vapor mixture might be expected, in the course of an ordinary thermodynamic process, to undergo a process of condensation or to increase its proportion in the mixture owing to evaporation. At least a part of that component would then be, occasionally, in the liquid phase. The mixture of gases is a pure substance, but gas-vapor mixtures cannot be so treated since the heavier liquid phase of the vapor will tend to settle, and the mixture will not be chemically homogeneous, as is required for classification as a pure substance. Examples of gas-vapor mixtures of engineering importance are atmospheric air, which is a mixture of the dry air of Chap. 9 with water vapor, the mixtures of fuel and air which are produced in the operation of the liquid-fuel carburetor, and the products of combustion resulting from the burning of a hydrogen-bearing fuel. Sometimes, for the purpose of more effective cooling, water is injected directly into the cylinder of an air compressor or an internal-combustion engine; its evaporation produces a gas-vapor mixture. Of these, the mixture of most general engineering interest is the air of the atmosphere, and a number of the special thermodynamic terms that are applied to gas-vapor mixtures in general are especially descriptive of atmospheric air. Because of this and since, in addition, atmospheric air is the gas-vapor mixture most familiar to the reader from the standpoint of personal observation of its behavior during changes in state, the discussion to follow is related directly to the moist-air mixture; the principles that develop will apply, in general, to many other gas-vapor mixtures.

Let a pan of water be placed in a room. A separation surface will be maintained between the water and the air above because of the liquid's property of surface tension. It will normally be observed that the amount of water in the pan gradually decreases, and it is evident that it must have escaped in the form of a vapor; yet no boiling of the liquid has taken place. The explanation is that the separation surface is not an impervious wall and therefore permits the passage of occasional molecules from among the immense number that strike it. This surface is bombarded from both sides—from below, by water molecules and, from above, by both the molecules of the air and those of the water vapor already present in that space. The air molecules cannot condense to form a liquid and therefore cannot pass the wall; the water-vapor molecules may occasionally pass and, as a result, become liquid molecules below the surface. At the same time, of course, liquid molecules from below the surface are escaping into the air above and so becoming vapor molecules.



If their rate of passage exceeds the rate at which vapor molecules assume the liquid phase, *evaporation* takes place; if the opposite is the case, *condensation* occurs, and the proportion of vapor molecules in the space above will decrease. These rates will depend upon the pressure exerted against the separation surface by the bombardment of the liquid and of the vapor molecules, respectively; when these pressures are balanced, the number of molecules escaping from the liquid will equal the number returning to the liquid and neither evaporation nor condensation will be observable, though an exchange of molecules will still be taking place.

The pressure exerted against the separation surface by the liquid molecules will depend upon their temperature; the pressure created by the vapor molecules is a function of both their temperature (assumed to be the same as the temperature of the liquid) and their concentration, increasing as that concentration increases. These pressures are balanced when the concentration of vapor molecules is such that their pressure is the saturation pressure corresponding to their temperature and the temperature of the liquid below the surface, according to the pressure-temperature relation (see Chap. 7) of the substance. For example, for water vapor at 70°F, this pressure is 0.3631 psia. This saturation pressure forms a part of the total pressure of the mixture of air and water vapor and is, of course, the partial pressure of the water vapor in that mixture. It is also the highest pressure possible for water vapor at the given temperature and therefore the highest partial pressure possible for the water vapor in an equilibrium mixture at that temperature. For if the vapor pressure were higher, condensation would take place until a state of equilibrium was attained. Thus the concentration of vapor molecules that is associated with the maximum vapor pressure is the maximum concentration that is possible in an air-water vapor mixture that is in equilibrium, and the air is said to be *saturated*. Note also that this concentration is the same as that which is characteristic of "saturated" vapor, in the sense in which that term was used in Chap. 7; the properties of the vapor portion of the mixture may therefore be obtained from tables of the properties of steam.

A summary of the conclusions reached in the preceding paragraph, as they apply to the general gas-vapor mixture which is in equilibrium with the liquid phase of its vapor component, leads to an extension of the Gibbs-Dalton law to include the following statement: *When a mixture of a gas and a vapor is in equilibrium with the liquid phase of the vapor component of the mixture, the density of the vapor is the same as the density of the pure vapor when in equilibrium with its liquid at the same temperature.*

Designating the vapor component as 1 and the gas as 2, Eqs. (10:1) to (10:7) may be applied to the *saturated* gas-vapor mixture, as follows:

$$\begin{aligned}
\frac{1}{v_m} &= \frac{1}{v_{g_1}} + \frac{1}{v_2} \\
p_m &= p_{g_1} + p_2 \\
U_m &= M_1 u_{g_1} + M_2 u_2 \\
H_m &= M_1 h_{g_1} + M_2 h_2 \\
S_m &= M_1 s_{g_1} + M_2 s_2
\end{aligned} \tag{10:19}$$

If component 2 is a mixture of gases instead of a single gas, the properties of that mixture may be assembled, by applying the methods of pages 205 to 207 of this chapter, before the properties of the gas-vapor mixture are investigated and this component can thereafter be treated as a single gas.

*Example 10:6.* A saturated atmospheric-air mixture has a total pressure of 14.7 psia and temperature of 70°F. Calculate the partial pressures of the water vapor and the dry air and the weight of water vapor per pound of dry air in the mixture. Find the volume, internal energy, enthalpy, and entropy of the mixture per pound of its dry-air content. Assume a reference level, corresponding to zero enthalpy and entropy, of 14.7 psia and 0°F for the dry-air portion, and, for the water vapor, use steam-table values.

*Solution.* Partial pressure of the water vapor =  $p_{g_1}$  = saturation pressure at 70°F = 0.3631 psia. Partial pressure of dry air =  $p_2 = p_m - p_{g_1} = 14.7 - 0.3631 = 14.34$  psia.  $V_m = v_2 = \frac{R_a T_a}{P_a} = \frac{(53.3)(530)}{(14.34)(144)} = 13.65$  ft<sup>3</sup> per pound of dry air.

$$v_{g_1} = 867.9 \text{ ft}^3/\text{lb} \text{ [Steam tables at 70°F]}$$

$$M_1 v_{g_1} = V_m \text{ or } M_1 = \frac{V_m}{v_{g_1}} = \frac{13.65}{867.9} = 0.0157 \text{ lb water vapor per pound of dry air}$$

$$H_m = M_1 h_{g_1} + M_2 h_2 = (0.0157)(1092.3) + (1)(0.24)(70 - 0) = 34 \text{ Btu}$$

At 14.7 psia and 0°F, the internal energy of 1 lb of dry air =  $h - \frac{Pv}{J} = 0 - \frac{RT}{J} = \frac{-(53.3)(460)}{778} = -31.4$  Btu. Then

$$U_m = M_1 u_{g_1} + M_2 u_2 = (0.0157)(1034.1) + 1[-31.4 + 0.170(70 - 0)] = -3.2 \text{ Btu}$$

Checking,

$$U_m = H_m - \frac{P_m V_m}{J} = 34 - \frac{(14.7)(144)(13.65)}{778} = 34 - 37.2 = -3.2 \text{ Btu}$$

$$s_2 = c_p \log_e \frac{T}{T_0} - \frac{R}{J} \log_e \frac{P}{P_0} = 0.24 \log_e \frac{530}{460} - \frac{53.3}{778} \log_e \frac{14.34}{14.7} = 0.0338 + 0.0017 = 0.0355$$

$$S_m = M_1 s_{g_1} + M_2 s_2 = (0.0157)(2.0647) + (1)(0.0355) = 0.0324 + 0.0355 = 0.0679$$

When the concentration of vapor molecules is less than the maximum, the vapor pressure is below the saturation pressure corresponding to the temperature of the mixture and the vapor component is therefore in the form of a superheated vapor. In Art. 7:9, it was pointed out that, at low pressures, lines of constant temperature on the Mollier chart become



horizontal, or constant-enthalpy, lines. This means that the enthalpy of the water vapor, like that of the perfect gas, is, for these pressures, a function of the temperature alone and suggests that, whether saturated or superheated, the water-vapor component of the atmospheric-air mixture may be treated as a perfect gas with negligible error. Thus the data of the steam tables may be extended to superheat states not shown in the table. The lowest pressure tabulated in Table 3 of the Keenan and Keyes tables is 1 psia, but the pressure of the superheated steam in the atmospheric-air mixture is usually much less than this pressure. From the above, the specific enthalpy (or the internal energy) of this superheated steam is the same as for saturated steam at the same *temperature*, and  $h_g$  at the temperature of the mixture may be substituted. As an example, suppose that an atmospheric-air mixture (not saturated) has a temperature of 80°F. Its water-vapor content is superheated steam, but neither its pressure nor its superheat is known. However, its specific enthalpy is 1096.6 Btu/lb, the value of  $h_g$  at 80°F, according to Table 1 of the Keenan and Keyes tables.

**10:7. Definitions.** In psychrometry,<sup>1</sup> a number of special terms are used to aid in the description of the state of the atmospheric-air mixture. Among those which we shall use are *specific humidity*, *relative humidity*, *dew point*, and *dry-bulb* and *wet-bulb temperature*. Although these terms are framed for application to the atmospheric-air mixture, they may also be used to good advantage in the description of the condition of any gas-vapor mixture.

*Specific humidity*  $\omega$  is the ratio of the mass of the water vapor to the mass of dry air in a given volume of the mixture. It may thus be expressed mathematically as

$$\omega = \frac{M_s}{M_a}$$

in which the subscript  $s$  refers to the water vapor (steam) and  $a$  to the dry-air component of the mixture. These occupy a common volume, so that  $M_s v_s = M_a v_a$ , or  $M_s/M_a = v_a/v_s$ . Treating both as perfect gases,  $v_a = R_a T_a/P_a = R_a T_m/P_a$ , and  $v_s = R_s T_s/P_s = R_s T_m/P_s$ . Substituting in the equation that defines  $\omega$ ,

$$\omega = \frac{M_s}{M_a} = \frac{v_a}{v_s} = \frac{R_a P_s}{R_s P_a} = \frac{53.3}{85.8} \frac{P_s}{P_a} = 0.622 \frac{p_s}{p_a} \quad (10:20)$$

in which  $p_s$  and  $p_a$  are the partial pressures of the water vapor and the air,<sup>2</sup> respectively.

<sup>1</sup> The science that deals with the behavior of mixtures of air and water vapor.

<sup>2</sup> The term air is here, and in following pages, used to refer to the mixture of gases, not including water vapor, which was given that name in Chap. 9. It is sometimes called *dry air*, for emphasis. Equation (10:20) may be applied to gas-vapor mixtures

The maximum specific humidity possible for atmospheric air at a given temperature and total (mixture) pressure is that associated with the saturated mixture. For saturated-atmospheric-air mixtures,  $p_s$  is the saturation pressure of steam that is equivalent to mixture temperature.

The *relative humidity*  $\phi$  is the ratio of the density of the water vapor in the mixture to its density in a saturated-atmospheric-air mixture at the same temperature, or

$$\phi = \frac{1/v_s}{1/v_g} = \frac{v_g}{v_s} = \frac{R_s T_m / P_g}{R_s T_m / P_s} = \frac{P_s}{P_g} = \frac{p_s}{p_g} \quad (10:21)$$

in which  $p_g$  is the saturation pressure of the vapor that corresponds to the temperature  $T_m$  of the mixture [see Eq. (10:19)]. If the mixture is saturated,  $p_s$  has its highest possible value for a given mixture temperature and is equal to  $p_g$ . The relative humidity of a saturated mixture is therefore 1.

When an atmospheric-air mixture, the water-vapor component of which is superheated steam, is cooled at constant pressure, its volume and temperature decrease and the superheat is gradually removed from the water vapor. During this process, the composition of the mixture does not change (its specific humidity is constant), and the partial pressures of both air and water vapor are (like that of the mixture as a whole) constant. Finally, a temperature is reached at which all of the superheat has been removed from the water-vapor component, and it is a saturated vapor. The mixture is also saturated, and any further cooling will result in progressive condensation of the vapor component. The temperature at which this condensation begins is called the *dew point* of the original mixture.

The statement that the partial pressure of the vapor is the same for the vapor as the saturation pressure corresponding to its dew point has been made above. This may be shown to be the case, based on the perfect-gas relation. The ratio  $M_s/M_m$  is constant during the cooling process that brings the mixture to its dew point. Then, for the mixture at any point in that cooling process,

$$\frac{P_s}{P_m} = \frac{M_s R_s T_s / V_s}{M_m R_m T_m / V_m} = \frac{M_s R_s T_m / V_m}{M_m R_m T_m / V_m} = \frac{M_s}{M_m} \frac{R_s}{R_m}$$

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other than atmospheric air if “gas” replaces “air” and “vapor” replaces “water vapor.” An equivalent change in the subscripts used in the equation from  $s$  to  $v$  and from  $a$  to “gas” might be appropriate, in that case. The constant 0.622 would change, of course, to the ratio  $R_{\text{gas}}/R_v$ . In giving Eq. (10:20) a more general application, in this manner, care should be observed that the pressures of the mixture components are low enough so that the perfect-gas relations, on which the equation is based, reflect the behavior of these components with sufficient accuracy.



$P_m$  is constant, and it follows, since  $R_s/R_m$  must be constant as long as the proportions of the mixture components do not change, that  $P_s$  is constant during the process; thus *the partial pressure of the water vapor in a mixture is its saturation pressure corresponding to the dew-point temperature*. This permits the substitution of this saturation pressure equivalent to the dew-point temperature for  $p_s$  in Eq. (10:21), thereby defining relative humidity on a new basis.

If the process discussed above is carried to temperatures below the dew point, condensation will have the effect of reducing the water-vapor content of the atmospheric-air mixture. This is one method by which the *dehumidification* of atmospheric air may be accomplished. The rate at which heat must leave the mixture to decrease the temperature a specified number of degrees will increase with the passing of the dew-point temperature, since the enthalpy of vaporization must be removed from the weight of vapor condensed in addition to the heat that must be removed from the remaining mixture to reduce its temperature. Thus the short-term temperature variation (as from day to night) to be expected in damp climates is normally considerably less than if the climate is dry.

If atmospheric air at a relative humidity less than 1 is brought into intimate contact with liquid water, some of the water will evaporate, with a resulting increase in the humidity of the mixture. Heat must be supplied to effect the vaporization of the liquid and comes from the mixing components, reducing their temperature. Advantage may be taken of this effect either to reduce the temperature of the atmospheric-air mixture, as in air conditioning by humidification, or to lower the temperature of the water, as when a cooling tower is used to provide a supply of cooled water. The process is called *adiabatic saturation* since, if the water and the atmospheric-air mixture are considered to constitute a single system, there has been no heat flow and because the limit to which the process may proceed is a saturation state for the mixture.

The process of adiabatic saturation is used for the experimental investigation of the humidity of the atmospheric-air mixture. Two thermometers, one of which is specially prepared by covering its bulb with a wetted wick, are placed side by side in a suitable frame and exposed to a stream of air. The *dry-bulb thermometer* will record the temperature of the air; its reading is called the *dry-bulb temperature*. Evaporation from the wick of the *wet-bulb thermometer* produces a saturated-air mixture in immediate contact with its bulb and a correspondingly lower temperature called the *wet-bulb temperature*. The amount by which the wet-bulb temperature is lower than the dry-bulb temperature is called the *wet-bulb depression* and is a qualitative measure of the capacity of the mixture for containing more water vapor, and thus of its dryness. Reference to standard tables or charts gives the corresponding relative humidity.

**Example 10-7A.** Find, for atmospheric air having a total pressure of 14.7 psia, a dry-bulb temperature of 80°F, and a relative humidity of 60 per cent ( $\phi = 0.6$ ), (a) the partial pressure of the water vapor, (b) the dew point, (c) the superheat of the water vapor, (d) the specific humidity, and (e) the enthalpy of the water vapor per pound of dry air in the mixture.

*Solution:*

(a)  $\phi = 0.6 = p_s/p_g$ , where  $p_g$  is 0.5069 psia, the saturation pressure at 80°F;  $p_s = (0.6)(0.5069) = 0.304$  psia;  $p_a = 14.7 - 0.304 = 14.396$  psia.

(b)  $p_s$  = saturation pressure at the dew-point temperature. Comparing in Table 1 of the steam tables, the dew point is found to be 64.8°F.

(c) The water vapor is superheated  $80 - 64.8 = 15.2^\circ\text{F}$ .

(d)  $\omega = 0.622(p_s/p_a) = 0.622(0.304/14.396) = 0.0131$  lb water vapor per pound of dry air.

(e) The specific enthalpy of the superheated water vapor is the same as that of saturated water vapor at the same temperature of 80°F, or 1096.6 Btu/lb (see Art. 10:6). Therefore  $H_s = M_s h_s = (0.0131)(1096.6) = 14.4$  Btu per pound of dry air in the mixture.

**Example 10-7B.** In the combustion of a fuel gas, to which reference is made in Example 10:3, the weight of water vapor formed per pound of the dry products of combustion is 0.118 lb. (a) When these products are cooled to 100°F at a pressure of 14.7 psia, what weight of water vapor has condensed? (b) The weight of the dry products is 19 lb per pound of fuel gas burned. How does the weight of water condensed compare with the weight of fuel burned?

*Solution:*

(a) The products can be assumed to be saturated. At 100°F,  $p_s = p_g = 0.9492$  psia. Then  $p_{\text{gas}} = 14.7 - 0.9492 = 13.75$  psia (note that  $p_{\text{gas}}$  is used since the dry portion of the mixture is not air).

$$\omega = \frac{R_{\text{gas}}}{R_s} \frac{p_s}{p_{\text{gas}}} = \frac{51.7}{85.8} \frac{p_s}{p_{\text{gas}}} = 0.602 \left( \frac{0.9492}{13.75} \right) = 0.0415 \text{ lb per pound dry products}$$

$$\text{Weight condensed} = 0.118 - 0.0415 = 0.0765 \text{ lb water per pound dry products}$$

$$(b) \text{ Ratio } \frac{\text{weight of water condensed}}{\text{weight of fuel burned}} = \frac{(19)(0.0765)}{1} = 1.45 \text{ lb per pound of fuel}$$

If the difference between the dry products of combustion and dry air had been ignored, the corresponding answers would have been (a) 0.0751 lb; (b) 1.43 lb.

**10:8. The Psychrometric Chart.** The solution of engineering problems that are concerned with atmospheric air is facilitated by the use of a chart which plots the specific humidity as ordinates vs. the dry-bulb temperature as abscissas. This is called a *psychrometric chart*; it is shown in skeleton form as Fig. 10:3, and a detailed psychrometric chart is included in the Appendix.

A psychrometric chart may be constructed for any total mixture pressure by applying the equations of the preceding articles; Fig. 10:3 and the chart in the Appendix are based on a total mixture pressure of 14.7 psia, standard atmospheric pressure. The first step in construction is the location of the saturation ( $\phi = 1.0$ ) curve, the locus of maximum specific



humidity corresponding to each temperature at the given total pressure. This may be accomplished by applying Eq. (10:20) substituting the saturation pressure corresponding to the dry-bulb temperature as  $p_s$  and with  $p_a = p_m - p_s$ . The  $\phi = 1.0$  line develops when the results of these computations are plotted and the points connected.

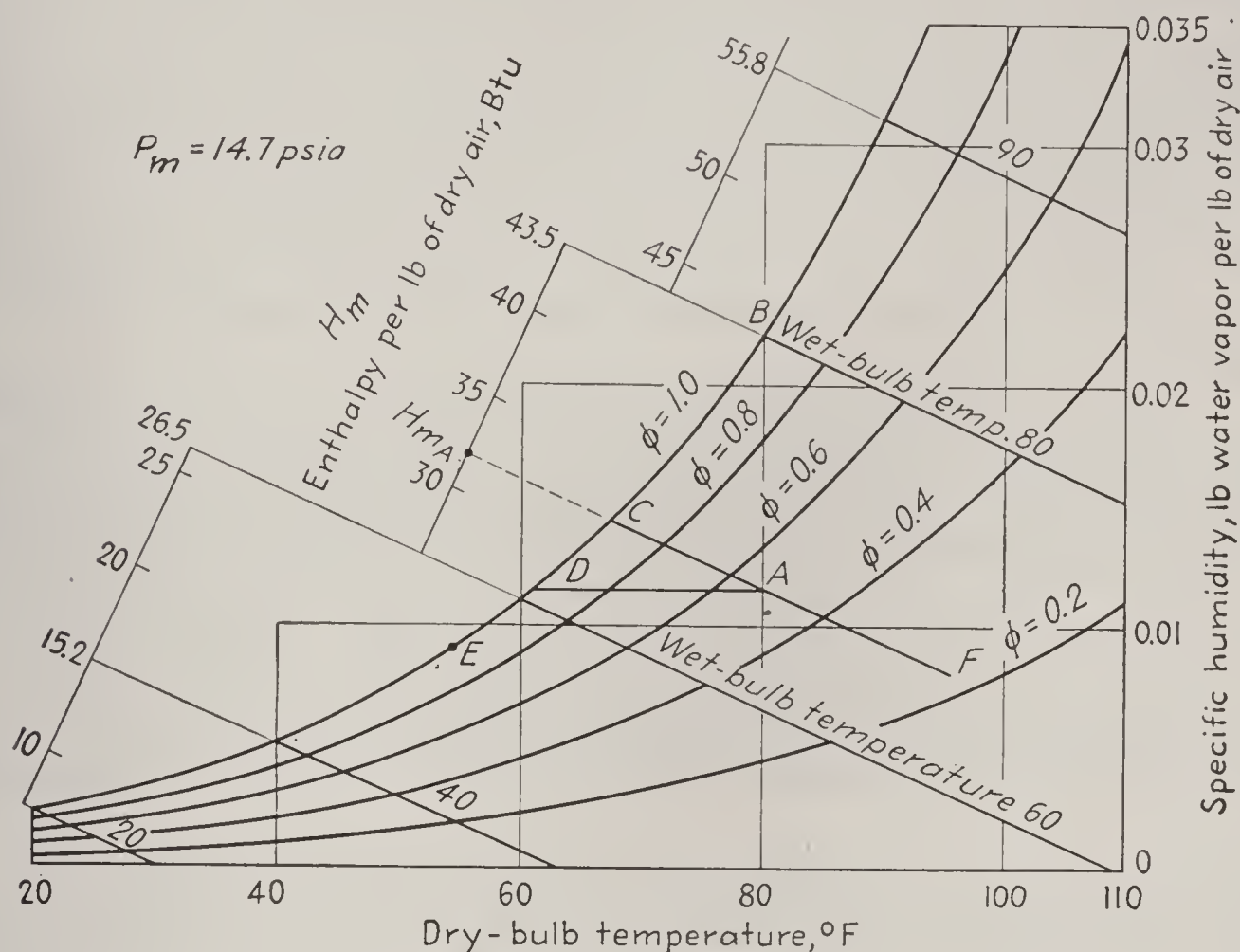


FIG. 10:3. Psychrometric chart.

The lines of constant relative humidity are next located; this may be done by applying Eq. (10:21), remembering that the saturation pressure of the water vapor at the dew-point temperature may be substituted for  $p_s$  in that equation. In Fig. 10:3, point *A* represents the assumed condition of an atmospheric-air mixture, having a dew point at *D*. Then  $\phi_A = p_{sA}/p_{gA} = p_{gD}/p_{gB}$ . Conversely, it is possible to locate point *A* so that  $\phi$  will have a certain value by finding the point *D* on the saturation curve at which the saturation pressure of the vapor is the equivalent fraction of the saturation pressure at *B* and placing *A* vertically below *B* and horizontally to the right of *D*.

Line *AC* represents a process of adiabatic saturation and is therefore a line of constant wet-bulb temperature. For saturated air, there is no wet-bulb depression, and the dry- and wet-bulb temperatures at point *C* are the same. Since the process is adiabatic, with no external work, Eq. (10:17) may be applied. Thus, if point *A* is to be located on a line of constant wet-bulb temperature passing through *C*,

$$\begin{array}{ccccc} (h_{aA} + \omega_A h_{gA}) & + & (\omega_C - \omega_A) h_{fA} & = & (h_{aC} + \omega_C h_{gC}) \\ \text{Enthalpy of mixture} & & \text{Enthalpy of water} & & \text{Enthalpy of mixture} \\ \text{at } A & & \text{to saturate} & & \text{at } C \end{array} \quad (10:22)$$

It has here been assumed that the water to saturate was supplied at the temperature of the mixture at  $A$ . Note also that, though the water-vapor portion of the mixture at  $A$  is really superheated steam, its specific enthalpy is denoted as  $h_{gA}$ , the enthalpy of the saturated vapor at temperature  $t_A$ ; the justification for this substitution was explained in Art. 10:6. The second term of the equation constitutes what would be called, in mathematics, an infinitesimal, since the difference  $\omega_C - \omega_A$  is a very small fraction of the total weight of the mixture and  $h_f$  is small as compared with  $h_g$ . This term is usually ignored and the equation written in the form

$$h_{aA} + \omega_A h_{gA} = h_{aC} + \omega_C h_{gC} \quad (10:23)$$

Thus, with the benefit of the simplification made possible by this approximation, lines of constant wet-bulb temperature become lines of constant mixture enthalpy. Accordingly, the lines of constant wet-bulb temperature may be extended to register on a scale of mixture enthalpies, as shown in Fig. 10:3. In supplying values for  $h_g$  and  $h_a$ , the standard practice is to use steam-table values for  $h_g$  and to assume a datum temperature of 0°F for the air portion of the mixture. Thus the enthalpy of the mixture at  $A$  is

$$H_{m_A} = h_{aA} + \omega_A h_{gA} = (1)(0.24)(t_A - 0) + \omega_A h_{gA} = 0.24t_A + \omega_A h_{gA} \quad (10:24)$$

The psychrometric chart in the Appendix shows the specific humidity in terms of grains (1 lb = 7000 grains) of water vapor per pound of dry air. The volume of an amount of the mixture that contains 1 lb of dry air is also shown. This may be determined if it is remembered that the volume of the mixture is the same as that of the dry air, and we may write

$$V_{m_A} = v_{a_A} = \frac{53.3T_A}{p_{a_A}} = \frac{53.3T_A}{P_m - P_{s_A}} \quad (10:25)$$

*Example 10:8.* The steps in the construction of a psychrometric chart similar to that in the Appendix are as follows: Construct (a) the saturation, or  $\phi = 1.0$ , line, (b) the constant relative-humidity curves, (c) the lines of constant wet-bulb temperature, (d) the enthalpy scale, and (e) the lines of constant volume. To illustrate the methods used in carrying out these steps, assume the total mixture pressure to be 14.7 psia, and calculate (a) the specific humidity of saturated air at 70°F, (b) the specific humidity of air at 80°F having a relative humidity of 60 per cent, (c) the specific humidity of air at 90°F dry-bulb and 70°F wet-bulb temperature, (d) the enthalpy of the mixture having a wet-bulb temperature of 70°F, and (e) the volume of the mixture, per pound of dry air, at 80°F, 60 per cent relative humidity. Compare the results with data read from the psychrometric chart in the Appendix. Note



that this comparison may be made only because the total mixture pressure is also 14.7 psia for that chart.

*Solution:*

(a) This calculation was made in Example 10:6. The specific humidity is 0.0157 lb water vapor per pound of dry air. The value as read from the chart in the Appendix is 110 grains, or  $\frac{110}{7000} = 0.0157$  lb.

(b) This calculation was made in Example 10:7A, where the specific humidity was shown to be 0.0131 lb. This agrees with the chart reading of 92 grains.

(c) Lines of constant wet-bulb temperature connect states having the same enthalpy of the mixture. For the saturated mixture, the wet- and dry-bulb temperatures are identical. The enthalpy of the mixture at the given state is therefore the same as for saturated air at a dry-bulb temperature of 70°F. This was shown to be 34 Btu in Example 10:6. We may write, for the assigned state,

$$H_m = 34 = h_a + \omega h_s = (0.24)(90) + \omega(1100.9) \text{ or } \omega = 0.0113 \text{ lb}$$

Note that  $h_g$  at 90°F has been substituted for the specific enthalpy of the (superheated) steam in the mixture. The chart reading is 78.5 grains, which checks closely.

(d) The enthalpy of the mixture at a wet-bulb temperature of 70°F is the same as that for a *saturated* mixture at a dry-bulb temperature of 70°F. This has been calculated as 34 Btu in Example 10:6. This agrees with the value shown on the chart.

(e) The volume of the mixture is the same as that of its components, or

$$V_m = v_a = \frac{R_a T_m}{P_a} = \frac{(53.3)(540)}{(14.396)(144)} = 13.9 \text{ ft}^3 \text{ per pound of dry air in mixture}$$

The value of  $p_a$  was calculated in Example 10:7A. The chart reading is about 13.89 ft<sup>3</sup>.

**10:9. Engineering processes for atmospheric air** are typically steady-flow in character, and Eq. (10:16) may be applied in the solution of the engineering problem. The basic processes may be classified as *heating or cooling at constant pressure* (ADE of Fig. 10:3), *humidification or dehumidification of saturated air* (DE), *adiabatic saturation* (humidification) (AC), and *adsorption*, or *adiabatic dehumidification* (AF).

*Heating at Constant Pressure.* This process could be demonstrated by passing the air over closed coils containing a warm fluid. The path on the psychrometric chart is horizontal (DA).

*Cooling at Constant Pressure.* This process has been discussed in the preceding article. The same method can be used as in heating, except that the coils are filled with a cold fluid. The path followed is AD and, if the process continues to temperatures below that at the dew point, DE. This part of the path also represents a *dehumidification of saturated air*.

*Humidification of Saturated Air.* Path ED could be traced by washing the air with warm water.

*Adiabatic saturation* has also been discussed above. It results when the air is washed with water at its own temperature. Path AC is followed.

In practice, the engineering process may be a combination of two or three of these basic processes. For example, if a large excess of chilled

water is used to wash the air, the path traced will be a compromise between  $ACD$  and  $AD$  down to the dew point and will thereafter proceed downward along the saturation curve to  $E$ . Thus dehumidification of the mixture may result from washing. Or a portion of the air may be cooled along path  $ADE$  and then remixed with the untreated portion, which has been by-passed around the cooling coils. By means such as this, the condition of the air may be changed to correspond to any desired point on the psychrometric chart.

The purpose of the engineering process may be to adjust the condition of the air, either for comfort or industrial use or, as in the case of the cooling tower, to cool the water with which the air is washed. Warm water enters at the top of the cooling tower and is sprayed downward into a rising stream of air. Atmospheric air enters at the foot of the tower and rises, owing either to convective effects or to the positive action of fans, against the downward flow maintained by the particles of liquid water because of their greater density. A small part of the water evaporates, increasing the humidity of the air and being carried off with it at the top of the tower. The balance of the water is cooled, largely by this evaporation, and may be drawn off at the bottom of the tower. The final temperature of the water may be less than the dry-bulb temperature of the entering air, depending on the relative rates of flow of air and water vapor, but cannot be less than its wet-bulb temperature.

*Example 10:9A.* Four thousand cubic feet per minute of air at 80°F dry-bulb, 70°F wet-bulb temperature is washed in a spray washer which is supplied with chilled water at 42°F. The air leaves the washer saturated at 50°F, and this is also the final temperature of the washing water. (a) What weight of cooling water must be supplied per hour? (b) What is the refrigeration (cooling) load in Btu per hour? (c) What volume of air leaves the washer per minute? (d) What weight of water is removed from the air per hour?

*Solution:*

(a) From the chart, at 80°F dry-bulb and 70°F wet-bulb,  $H_m = 34$  Btu,  $V_m = 13.89$  ft<sup>3</sup>,  $\omega = 94$  grains. For saturated air at 50°F,  $H_m = 20.3$  Btu,  $V_m = 13.0$  ft<sup>3</sup>,  $\omega = 54$  grains. All values are per pound of dry air in the mixture. The specific enthalpy of the cooling water at entrance to the washer is 10.05 Btu and, at exit, 18.07 Btu/lb ( $h_f$  at 42 and 50°F, respectively). The weight of dry air handled is

$$\frac{4000}{13.89} = 288 \text{ lb/min}$$

The washing process is an adiabatic no-work steady-flow mixing process. The kinetic energy and elevation terms of Eq. (10:16) may be disregarded and Eq. (10:17) employed. Substitution in this equation will be made with  $M_i$ , representing the weight of the cooling water supplied per pound of dry air in the entering atmospheric mixture. Since the outgoing weight of cooling water must be greater than its initial weight by the weight of water vapor condensed from the air,



$$M_{o1} = M_{i1} + \frac{94 - 54}{7000} = M_{i1} + 0.0057$$

$$M_{i1}h_{i1} + H_{m_i} = M_{o1}h_{o1} + H_{m_o} \text{ or } M_{i1}(10.05) + 34.0 = (M_{i1} + 0.0057)(18.07) + 20.3$$

Solving,

$M_{i1} = 1.695$  lb of cooling water supplied per pound of dry air in mixture. This corresponds to a flow of  $(1.695)(288)(60) = 29,300$  lb/hr.

(b) The refrigeration load, based on the heat that must be removed from the water to recool it to  $42^\circ\text{F}$ , is  $29,300(18.07 - 10.05) = 235,000$  Btu/hr. This could also have been calculated as the enthalpy loss of the air, or  $(288)(60)(34.0 - 20.3) = 237,000$  Btu/hr. The discrepancy between the two answers results from neglecting, in the second computation, the enthalpy of the water that was condensed from the air.

(c) Volume of air leaving washer  $= (288)(13.0) = 3750$  cfm

(d) Water removed from air  $= (0.0057)(288)(60) = 98.5$  lb/hr

The difference in the two answers to part b was approximately 2000 Btu/hr. This difference is, more accurately,  $(98.5)(18.07) = 1780$  Btu/hr.

*Example 10:9B.* If, in Example 10.9A, the air issuing from the washer had been remixed with 2000 cfm of air that had been by-passed around the washer, determine the properties of the resulting mixture.

*Solution:*

$$\text{Weight of dry air by-passed} = \frac{2000}{13.89} = 144 \text{ lb/min}$$

$$\text{Enthalpy of resultant mixture} = \frac{(144)(34.0) + (288)(20.3)}{144 + 288} = 24.8 \text{ Btu per pound of dry air}$$

$$\text{Its specific humidity} = \frac{(144)(94) + (288)(54)}{144 + 288} = 67.3 \text{ grains per pound of dry air}$$

The calculated enthalpy is taken to the chart and found to correspond to a wet-bulb temperature of about  $57.5^\circ\text{F}$ . The intersection of this wet-bulb-temperature line with a specific humidity of 67.3 grains gives a dry-bulb temperature of about  $60^\circ\text{F}$ . Since the enthalpy and specific-humidity scales are linear, this intersection will lie on a line joining the states of the uniting mixtures on the psychrometric chart. Other properties of the resultant mixture may be read from the chart as  $V_m = 13.3 \text{ ft}^3$ ;  $\phi = 0.87$ ; dew point  $= 56^\circ\text{F}$ .

*Example 10:9C.* Water enters the top of a cooling tower at  $110^\circ\text{F}$  and is cooled to  $70^\circ\text{F}$  as it falls to the bottom. Air enters the bottom at  $75^\circ\text{F}$  and a relative humidity of 40 per cent and leaves at the top at  $105^\circ\text{F}$ , relative humidity 95 per cent. Calculate (a) the weight of water cooled per pound of dry air passing through the tower and (b) the per cent of cooling water lost by evaporation.

*Solution:*

(a) At  $105^\circ\text{F}$ ,  $\phi = 0.95$ , the partial pressure of the water vapor is  $(0.95)(1.1016) = 1.048$  psia. The specific humidity of the air as it leaves is

$$\omega_o = 0.622 \left( \frac{1.048}{14.7 - 1.048} \right) = 0.0477 \text{ lb per pound of dry air}$$

$$H_{m_o} = (0.24)(105) + (0.0477)(1107.3) = 78.0 \text{ Btu per pound of dry air.}$$

At entrance, the specific humidity, as read from the chart, is 51.5 grains, or 0.0074 lb per pound of dry air, and the enthalpy is 26.3 Btu.<sup>1</sup>

<sup>1</sup> The General Electric Company psychrometric chart shown in the Appendix calls this the total heat instead of the enthalpy. This conforms to an earlier practice, now

The specific enthalpy of the water is 77.94 Btu/lb at the top and 38.04 Btu/lb at the bottom of the tower.

Equation (10:17) will apply and, for unit weight of dry-air flow,

$$M_{i_1}(77.94) + (1)(26.3) = [M_{i_1} - (0.0477 - 0.0074)](38.04) + (1)(78.0)$$

from which

$$M_{i_1} = 1.26 \text{ lb of water cooled per pound of dry air through the tower}$$

$$(b) \text{ Per cent of water lost by evaporation} = \left( \frac{0.0477 - 0.0074}{1.26} \right) (100) = 3.2 \text{ per cent}$$

### Problems

1. A mixture has the following proportions by volume: CO<sub>2</sub>—13 per cent; O<sub>2</sub>—6 per cent; N<sub>2</sub>—81 per cent. Its pressure is 25 psia and its temperature 100°F. The internal energy and the entropy are arbitrarily zero for each gas existing separately at 14.7 psia and 32°F. Find (a) the apparent molecular weight and the gas constant of the mixture, (b) the gravimetric analysis, (c) the specific internal energy, enthalpy, and entropy of the mixture, (d) the partial pressure of each constituent, (e) the specific volume of the mixture, and (f) the ratio  $k$  for the mixture.

2. A mixture at 25 psia and 100°F has the following gravimetric analysis: CO<sub>2</sub>—50 per cent; O<sub>2</sub>—40 per cent; helium—10 per cent. Find (a) its apparent molecular weight and gas constant, (b) its specific volume, (c) the mole fractions of its components, (d) their partial pressures, and (e) the exponent  $k$  for reversible adiabatic expansion.

3. Substitute the following mixtures (percentages by volume) for the mixture of Prob. 1, and find the same quantities: (a) N<sub>2</sub> 50 per cent and O<sub>2</sub> 50 per cent; (b) CO<sub>2</sub> 50 per cent and O<sub>2</sub> 50 per cent; (c) He 50 per cent and O<sub>2</sub> 50 per cent.

4. Substitute the following mixtures (percentages by weight) for the mixture of Prob. 2, and find the same quantities: (a) N<sub>2</sub> 50 per cent and O<sub>2</sub> 50 per cent; (b) CO<sub>2</sub> 50 per cent and O<sub>2</sub> 50 per cent; (c) He 50 per cent and O<sub>2</sub> 50 per cent.

5. A mixture consists of 0.2 mole of nitrogen, and the balance is helium. Its total pressure is 100 psia, and its volume is 20 ft<sup>3</sup>. The partial pressure of the helium is 40 psia. What is the temperature of the mixture?

6. The combustion equation for methane is  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ . What is the specific volume of a mixture of methane with just enough oxygen to support complete combustion if the pressure of the mixture is 14.7 psia and its temperature is 70°F? If  $c_v$  for methane is 0.45 Btu/(lb)(°F), what is the exponent  $k$  for reversible adiabatic compression for this mixture?

7. In Prob. 6, change the mixture to a mixture of methane with just enough air to furnish the oxygen for its complete combustion. If air is a mixture of 3.29 lb of nitrogen per pound of oxygen, calculate the gas constant of the mixture. What is the ratio of the specific heats,  $k$ ?

8. Tank 1 has an internal volume of 4 ft<sup>3</sup>, tank 2 a volume of 6 ft<sup>3</sup>. The pressure and temperature of the contents of each tank are 14.7 psia and 32°F. The two tanks are connected, and their contents are allowed to form a mixture at a common temperature and pressure. Describe the composition of the resulting mixture in terms of the mole fractions of its components, state the pressure and temperature of the mixture

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almost never seen. The confusion that might be caused in the student's mind by the use of "total heat" is obvious. The term enthalpy was devised for the purpose of eliminating that confusion.



that results from adiabatic mixing, and calculate the change of entropy that takes place, if the tanks originally held, respectively, (a) nitrogen and oxygen, (b)  $\text{CO}_2$  and  $\text{O}_2$ , (c) helium and  $\text{O}_2$ ; (d) if both tanks contained oxygen. In each case, is the mixing process reversible?

9. The same as Prob. 8, except that the pressure differs in the two tanks before they are connected. For tank 1 it is 20 psia; for 2 it is 15 psia. The temperature remains at  $32^\circ\text{F}$  initially in both tanks. For gas combinations as described in Prob. 8, answer the same questions.

10. Same as Prob. 8, except that the temperature differs in the two tanks before they are connected. For tank 1 it is  $50^\circ\text{F}$ ; for tank 2 it is  $32^\circ\text{F}$ . The pressure is initially 14.7 psia in both tanks. For gas combinations as described in Prob. 8, answer the same questions.

11. Work Example 10:4, changing the amounts of each gas from 1 lb. to 1  $\text{ft}^3$  in each compartment. Answer the same questions.

12. As they pass through the mixing valve on the way to the cylinder of an internal-combustion engine, a steady stream of methane (see Probs. 6 and 7) at  $70^\circ\text{F}$  is mixed with a steady stream of air at  $90^\circ\text{F}$ . The proportionate rates of flow are such that the air will contain just enough oxygen for complete combustion of the methane. What is the resultant temperature of the mixture? Assume the mixing to be adiabatic and the velocities of the methane and the air entering and of the mixture leaving the valve to differ negligibly.

13. In Prob. 12, let the velocity of the air entering and the mixture leaving the valve be 20 fps, while the methane enters at 400 fps. Heat enters through the walls that confine the flow between the two sections at the rate of 50 Btu per pound of methane entering the mixture. What is the temperature of the mixture?

14. A gas mixture is composed of 20 per cent  $\text{CO}_2$ , 30 per cent  $\text{O}_2$ , and 50 per cent  $\text{N}_2$  by weight. In steady flow through a heat exchanger, its pressure decreases from 20 to 15 psia and its temperature from  $220$  to  $130^\circ\text{F}$ . Differences in velocity and in elevation between entrance and exit are negligible. Find the amount of heat transferred per pound of the mixture. What is the change of entropy per pound?

15. Ten thousand pounds per hour of water at  $80^\circ\text{F}$  enters an open feedwater heater, where it comes in contact with steam at 14.7 psia and a quality of 0.90. If the resulting mixture is withdrawn at  $210^\circ\text{F}$  at a rate such that the liquid level in the heater is constant, how many pounds leave the heater per hour?

16. A mixture is composed of equal percentages by weight of carbon dioxide and helium. It is compressed reversibly and adiabatically from 14.7 psia,  $70^\circ\text{F}$ , to a final pressure of 75 psia. How much work is required per pound of the mixture? Per pound of the mixture, what are the individual entropy changes of each constituent?

17. The same as Prob. 16, except that the percentages are equal by volume.

18. Work Example 10:6 for the following temperatures and total pressures of the saturated-atmospheric-air mixture: (a)  $90^\circ\text{F}$  and 14.7 psia; (b)  $90^\circ\text{F}$  and 10 psia; (c)  $70^\circ\text{F}$  and 10 psia. What conclusions do you draw as to the effect of temperature on the mole fraction of water vapor in the saturated-air mixture? As to the effect of total mixture pressure?

19. In Prob. 7 assume the combustion of the methane to be complete, *i.e.*, to be represented by the combustion equation of Prob. 6. What are the weights of, respectively,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  in the products per mole of methane burned? When these products have a total pressure of 14.7 psia and a temperature of  $70^\circ\text{F}$ , what fraction of the total weight of  $\text{H}_2\text{O}$  which was formed must have condensed? What are the partial pressures of the gaseous components of the products at the stated temperature and total pressure?

20. Based upon the steam-table convention as to the reference level from which enthalpy is measured, find the specific enthalpy of steam at the states described as follows: (a)  $p = 0.10$  psia,  $t = 60^\circ\text{F}$ ; (b)  $p = 0.10$  psia,  $t = 80^\circ\text{F}$ ; (c)  $p = 0.20$  psia, superheated  $30^\circ\text{F}$ .

21. Water is allowed to evaporate into an "atmosphere" of pure hydrogen until a saturated mixture results. If the temperature and pressure of this mixture are  $70^\circ\text{F}$  and  $14.7$  psia, what is its specific humidity? What are the mole fractions of its components? If the "atmosphere" is carbon dioxide, what are the similar values?

22. In Example 10:7A, change the total pressure to  $10$  psia, and find the same properties.

23. Find the specific volume of steam at the states listed in Prob. 20.

24. Atmospheric air has a total pressure of  $14.7$  psia, a temperature of  $50^\circ\text{F}$ , and a relative humidity of  $40$  per cent. Find (a) the partial pressure of the water vapor; (b) the dew point; (c) the superheat of the water vapor; (d) the specific humidity; (e) the enthalpy of the water vapor per pound of dry air in the mixture.

25. The total pressure of the air in a heated room is  $14.7$  psia. At the center of the room the temperature of the air is maintained at  $70^\circ\text{F}$  and its relative humidity at  $50$  per cent, but near an exposed wall the temperature is lower owing to a flow of heat outward through the wall. How low may be the temperature at the wall without resulting in a condensation of moisture on that surface?

26. In Example 10:7A, calculate the wet-bulb temperature. Change the total pressure to  $10$  psia (as in Prob. 22), and again calculate the wet-bulb temperature. Compare your calculations for the two pressures. Do you obtain different answers for the two pressures, and if so, what causes the difference?

27. A mixture of hydrogen and water vapor has a pressure of  $14.7$  psia and a temperature of  $70^\circ\text{F}$ . Its relative humidity is  $60$  per cent. (a) What is the partial pressure of the water vapor? (b) What is the dew point? (c) What is the specific humidity? (d) What is the wet-bulb temperature? Repeat for a mixture of carbon dioxide and water vapor at the same pressure, temperature, and relative humidity.

28. Atmospheric air at  $14.7$  psia and  $80^\circ\text{F}$  has a wet-bulb temperature of  $50^\circ\text{F}$ . Calculate (a) its specific humidity; (b) its dew point; (c) its relative humidity. Change the total pressure to  $10$  psia, and calculate the same properties.

29. Using the psychrometric chart, solve Probs. 24, 25, 26, and 28. Check the solution of Example 10:7A. Can the chart be used for the solution of Prob. 22? For the solution of Prob. 27?

30. A saturated mixture of hydrogen and ammonia vapor has a pressure of  $180$  psia and a temperature of  $0^\circ\text{F}$ . What are the partial pressures of its components? What are their percentages by weight in the mixture?

31. Given air at a dry-bulb temperature of  $80^\circ\text{F}$  and having a dew point of  $70^\circ\text{F}$ , read the following from the psychrometric chart: (a) relative humidity; (b) wet-bulb temperature; (c) specific humidity; (d) enthalpy; (e) volume. What restriction, if any, applies to the use of these values?

32. Air at  $88^\circ\text{F}$  and  $40$  per cent relative humidity is humidified adiabatically as it passes through a washer. What is its final temperature as it leaves the washer as saturated air? Use the psychrometric chart. What is the change in specific humidity?

33. Air at  $88^\circ\text{F}$  and  $40$  per cent relative humidity is passed through cooling coils in which its temperature is lowered until the air becomes saturated. What is the final temperature? How much heat is removed per pound of dry air? Use the chart.

34. Fourteen hundred cubic feet per minute of air at  $85^\circ\text{F}$  dry-bulb temperature and  $50$  per cent relative humidity is mixed with  $200$  cfm of air at  $54^\circ\text{F}$  dry-bulb temperature and  $40$  per cent relative humidity. Based on values read from the chart,



find the resulting dry-bulb temperature, wet-bulb temperature, and relative humidity.

35. How many cubic feet per minute of air at 70°F dry-bulb temperature and 50 per cent relative humidity must enter a cooling tower to cool 100 gal of water per minute from 85 to 70°F, assuming that the air is saturated at 80°F as it leaves the top of the tower?

36. An evaporative cooler is used to cool a residence in the summer. The cooler draws 3400 cfm of outside air with a dry-bulb temperature of 92°F and a relative humidity of 20 per cent. While in the cooler, the air is sprayed with water until, when discharged into the house, its relative humidity has been increased (adiabatically) to 90 per cent. How many pounds of water are evaporated into the air per minute? What is the final dry-bulb temperature of the air?

37. Ten thousand cubic feet per minute of air at 60°F dry-bulb temperature and 40 per cent relative humidity is passed over a cooling coil. Assuming that the air leaves the coil at 55°F dry-bulb temperature, how many Btu are removed per hour by the coil?

38. Find the weight of dry air that must be drawn hourly through a cooling tower to cool 60,000 lb of water per hour from 105 to 75°F if the air enters at 70°F and with a relative humidity of 30 per cent and leaves at 100°F and a relative humidity of 95 per cent. What percentage of the water is evaporated?

39. The *absolute humidity* of moist air is the weight of water vapor per cubic foot of air. Construct a psychrometric chart on which the absolute humidity is plotted as the ordinate vs. dry-bulb temperatures as abscissas, plotting the following loci: 100 per cent relative humidity, 50 per cent relative humidity. Note that these loci are independent of the total pressure of the mixture. Assuming the total pressure to be 14.7 psia, plot the line which represents a constant wet-bulb temperature of 70°F.

40. Construct a skeleton psychrometric chart similar to Fig. 10:3 but based on a total atmospheric pressure of 24.89 in. Hg (equivalent to an altitude of 5000 ft above sea level). Take the following steps in order: (a) Calculate data for saturation (100 per cent relative humidity) curve at 10°F intervals, and plot. (b) Based on the dew-point temperature, calculate data for the 50 per cent relative humidity line, and plot. (c) Calculate necessary data, and plot a line of 70°F wet-bulb temperature. (d) Determine the locus of conditions for which the total volume of the standard unit mixture is 16 ft<sup>3</sup>, and plot this locus on the chart.

### Symbols

$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$C$	a constant
$g$	acceleration of gravity
$h$	enthalpy of unit mass
$H$	enthalpy of a system
$J$	proportionality factor
$k$	ratio of the specific heats, $c_p/c_v$
$m$	molecular weight; weight of 1 mole
$M$	mass; mass rate of flow
$n$	a constant
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow

$R$	gas constant
$s$	entropy of unit mass
$S$	entropy of a system
$T$	absolute temperature
$u$	internal energy of unit mass
$U$	internal energy of a system
$v$	specific volume
$V$	volume of a system
$\bar{V}$	velocity
$W$	rate of work delivery
$x$	mole fraction of a component in a mixture
$z$	elevation

*Greek Letters*

$\phi$	relative humidity
$\omega$	specific humidity

*Subscripts*

$a$	air
$e$	natural logarithmic base
$g$	of the saturated vapor
$i$	incoming
$m$	mixture
$o$	outgoing
$p$	constant pressure
$s$	steam; water vapor
$v$	constant volume



## CHAPTER 11

### STEADY FLOW OF FLUIDS—THE TURBINE

**11:1. Introduction.** A study of the behavior of fluids in steady flow is useful in the analysis of optimum performance of turbines and other devices that utilize a fluid in steady flow, in the design of these units, in the design of pipes and ducts for conveying fluids, and in the measurement of fluid flow. All of these are purposes that may be of major importance to the engineer. Only those aspects which are concerned with the turbine and similar devices will be treated in the present chapter.

All real fluids have the property called viscosity in greater or in less degree. The flow of a viscous fluid can never be reversible, but it will be our policy to discuss first the limiting, or reversible, process, ignoring viscosity. The discrepancies between ideal and actual performance will then be noted. For example, there will be no drop in pressure along a horizontal pipe or duct of constant cross-sectional area which carries a nonviscous fluid in adiabatic flow, and the fluid will issue from the passage in exactly the same state as when it enters; nor will any work be required for its transport. This varies widely from the conditions encountered in real flow through such lines, and these conditions cannot be predicted until viscosity is taken into account.

The basic tools for the analysis of the behavior of the fluid in steady flow are the steady-flow energy equation [Eq. (3:5)] and the continuity equation of steady flow [Eq. (3:8)]. For ease of reference, these equations will be repeated here.

$$h_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} + {}_1Q_2 = h_2 + \frac{\bar{V}_2^2}{2Jg} + \frac{z_2}{J} + \frac{{}_1W_2}{J} \quad (3:5)$$

$$M_1 = M_2 = \frac{A_1 \bar{V}_1}{v_1} = \frac{A_2 \bar{V}_2}{v_2} \quad \text{or} \quad M = \frac{A \bar{V}}{v} \quad (3:8)$$

These two equations apply to the steady flow of fluids whether that flow is reversible or irreversible. They may also be used, with certain limitations, when the flow is not strictly steady in character (see Art. 3:9).

The turbine is not a heat engine; as the prime mover, it may form a part of the steady-flow heat engine (see Art. 3:8 and Fig. 3:4). In the turbine, a dual operation is carried out. The fluid is first given increased velocity by reducing its pressure as it passes through a constricted passageway, called a *nozzle*, and this kinetic energy is then removed, by

means of moving blades, or *buckets*, to reappear as shaft work; the velocity may be partly generated in the passages between the buckets themselves. The turbine principle may be applied whether the fluid is a vapor, a gas, or a liquid. The steam turbine is perhaps most familiar to the average engineer, and its operating principle is sketched in Fig. 11:1. The figure shows a very simple type of the steam turbine, which is built in a multitude of forms, but serves to illustrate the general principle of operation of all turbines, whether steam, water, or gas. The analysis of optimum turbine performance is carried out by first analyzing the flow through the

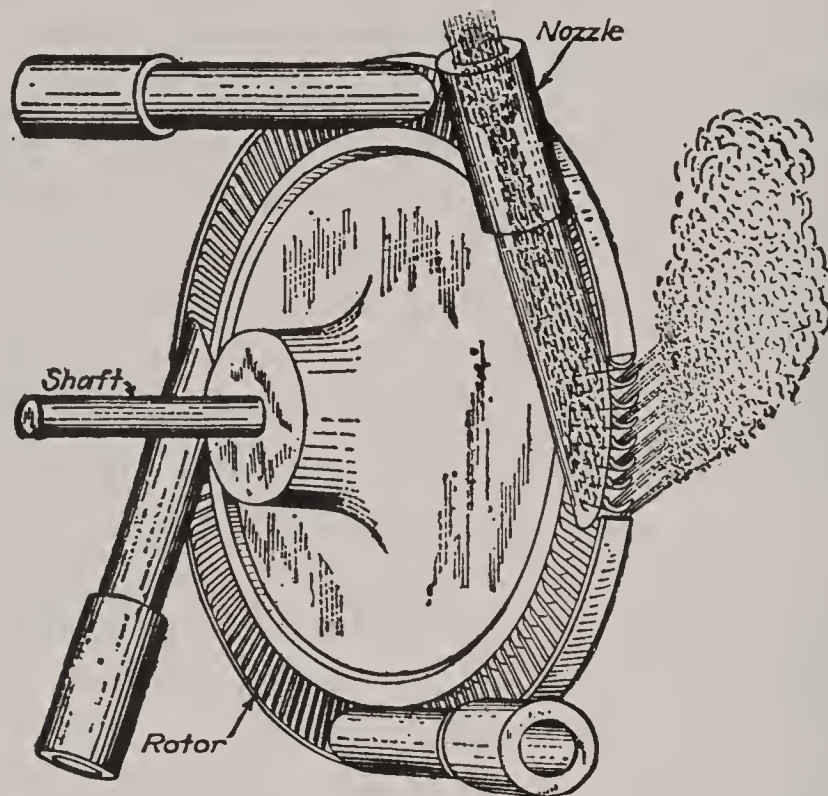


FIG. 11:1. DeLaval steam turbine.

nozzle and then the flow through the bucket which converts the kinetic energy of the jet into shaft work, these flows being treated as reversible (frictionless) in character.

**11:2. The Reversible Adiabatic Nozzle.** The flow through the nozzle is assumed to be adiabatic because the brief time required for passage from entrance to exit gives little opportunity for appreciable heat flow. Because limiting, or reversible, flow is the subject of our study at present, the flow is also isentropic. This establishes a relationship between  $h_1$  and  $h_2$  in Eq. (3:5) since it requires that the entropies  $s_1$  and  $s_2$ , at entrance and exit, respectively, shall be equal. The differences in elevation between entrance and exit are insignificant, and the elevation terms in the equation may be dropped. No external work is performed in the nozzle, and we may rewrite Eq. (3:5), as it applies to the reversible nozzle, as

$$\frac{\bar{V}_2^2}{2Jg} - \frac{\bar{V}_1^2}{2Jg} = (h_1 - h_2)_s \quad (11:1)$$

in which the enclosure of the enthalpy difference and the use of the sub-



script  $s$  reminds us of the isentropic character of the flow. In the nozzle, the object is to increase the velocity of flow, and  $\bar{V}_2 > \bar{V}_1$ ; a decrease of enthalpy must take place, and  $h_1 > h_2$ . When the velocity ratio  $\bar{V}_2/\bar{V}_1$  is large, it is often possible to drop  $\bar{V}_1^2/2Jg$  from this equation as an approximation; for example, if  $\bar{V}_2/\bar{V}_1 = 20$ , then  $\bar{V}_2^2 = 400\bar{V}_1^2$  and the error invited amounts to only one-fourth of 1 per cent. If this approximation is employed, Eq. (11:1) simplifies to

$$\bar{V}_2 = [2Jg(h_1 - h_2)_s]^{\frac{1}{2}} = 223.8[(h_1 - h_2)_s]^{\frac{1}{2}} \quad (11:2)$$

Assuming that the state of the fluid at entrance to the nozzle is known, including the initial pressure  $p_1$ , and that we have adequate information as to the relation between the properties of the fluid (as, perhaps, in the form of an equation of state or a table of properties), it is possible to establish the state at exit if  $p_2$  is known, since one other property ( $s_2$ ) corresponding to that state is also known. These calculable properties will, of course, include  $h_2$  and  $v_2$ . We are now in a position to apply Eq. (11:1) or Eq. (11:2) to the calculation of  $\bar{V}_2$ . Next, from Eq. (3:8),

$$A = \frac{Mv}{\bar{V}} \quad (11:3)$$

and the cross-sectional exit area required for a given rate of fluid flow can be computed by substituting the previously determined values of  $v_2$  and  $\bar{V}_2$  in this equation.

The flow is isentropic at all sections of the nozzle, and if it becomes desirable to calculate the cross-sectional area of the nozzle at some intermediate station  $a$ , where the pressure  $p_a$  has some known value between  $p_1$  and  $p_2$ , the same methods may be applied to the calculation of  $A_a$ .

**11:3. The Liquid Nozzle.** It may be shown that, during the isentropic process,

$$dh = d\left(u + \frac{Pv}{J}\right) = du + \frac{P dv}{J} + \frac{v dP}{J} = T ds + \frac{v dP}{J} = \frac{v dP}{J}$$

This is the basis of a convenient method of calculating the change of enthalpy of an incompressible fluid during isentropic flow. Liquids are compressible in such small degree that we may safely consider  $v$  to be constant in connection with the liquid nozzle. Thus, substituting in Eq. (11:1),

$$\frac{\bar{V}_2^2}{2Jg} - \frac{\bar{V}_1^2}{2Jg} = (h_1 - h_2)_s = - \int_1^2 dh = - \frac{v}{J} \int_1^2 dP = \frac{v}{J} (P_1 - P_2)$$

or

$$\frac{\bar{V}_2^2}{2g} - \frac{\bar{V}_1^2}{2g} = v(P_1 - P_2) \quad (11:4)$$

indicating that the increase of kinetic energy of the liquid, as it flows through the nozzle, is proportional to the drop in pressure.

In Eq. (11:3),  $M$  and  $v$  are both constants for liquid flow and a continuous decrease in nozzle cross-sectional area in the direction of flow is evident if the velocity is continuously to increase. This is a *converging nozzle* such as is illustrated in Fig. 11:2. The shape of the walls here shown is such as to make the rate of velocity change per unit length of channel larger near the entrance, where the velocities are low, and smaller near the exit. This is found to give good results in the real nozzle, for which frictional effects must be considered. The reversible adiabatic



FIG. 11:2. Converging nozzle.

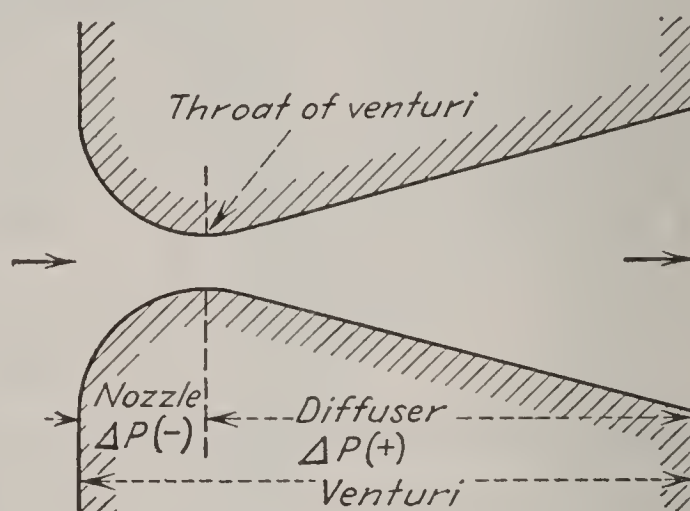


FIG. 11:3. The venturi.

nozzle may be designed to give equal increments of velocity, of kinetic energy, or equal pressure drop per unit of nozzle length, as desired. The real nozzle should be shaped to give a minimum of irreversibility (friction) in flow of the fluid; its proportions are based on the results of experimental observation.

If the liquid, having reached the exit section of the converging nozzle shown in Fig. 11:2, is then caused to enter a diverging passageway which ultimately reaches, in its cross section, the inlet area of the converging nozzle, as shown in Fig. 11:3, a *venturi* is formed. The section of this venturi downstream from the *throat of the venturi*, its smallest section, is called a diffuser. The pressure rises in the direction of flow in a diffuser, and if the flow is adiabatic and reversible and the areas at entrance to and exit from the venturi are equal, the pressure of the liquid at exit from the diffuser will have been built up to equal that at entrance to the nozzle and all other properties at these two sections will also be the same. The viscosity of a real fluid will produce frictional effects that will make reversible flow impossible, and the pressure at exit from the diffuser will fall somewhat short of equaling that at entrance to the nozzle section of the venturi. The comparison of the pressure loss between these two



sections, when equivalent flow conditions are maintained, furnishes one means of comparing the viscosities of fluids.

*Example 11:3.* A water nozzle is to be designed to discharge 10,000 lb of water per minute at a velocity of 150 fps and to connect to a line having an internal diameter of 6 in. Assuming discharge is to the atmosphere and neglecting friction, calculate (a) the diameter of the nozzle at its exit and (b) the pressure and velocity of the water in the line as it approaches the nozzle.

*Solution:*

$$(a) \quad A_2 = \frac{Mv_2}{\bar{V}_2} = \frac{10,000}{(60)(62.4)(150)} = 0.0178 \text{ ft}^2 = 2.56 \text{ in.}^2$$

$$\text{Diameter at exit} = D_2 = \left( \frac{4A_2}{\pi} \right)^{\frac{1}{2}} = \left( \frac{2.56}{0.7854} \right)^{\frac{1}{2}} = 1.81 \text{ in.}$$

$$(b) \quad \bar{V}_1 = \frac{Mv_1}{A_1} = \frac{(10,000)(144)}{(60)(62.4)(0.7854)(36)} = 13.6 \text{ fps}$$

Substituting in Eq. (11:4),

$$\frac{150^2}{64.4} - \frac{13.6^2}{64.4} = \frac{144}{62.4} (p_1 - 14.7) \text{ or } p_1 = 170 \text{ psia}$$

**11:4. The Perfect-gas Nozzle.** For the perfect gas,

$$\begin{aligned} (h_1 - h_2)_s &= c_p(T_1 - T_2)_s = \frac{k}{k-1} \frac{R}{J} (T_1 - T_2)_s \\ &= \frac{k}{k-1} \frac{RT_1}{J} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{(k-1)/k} \right] \end{aligned} \quad (11:5)$$

Making this substitution in Eq. (11:1), we have

$$\frac{\bar{V}_2^2}{2g} - \frac{\bar{V}_1^2}{2g} = Jc_p(T_1 - T_2)_s = \frac{k}{k-1} RT_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{(k-1)/k} \right] \quad (11:6)$$

As the pressure of a gas decreases during flow through a nozzle, the specific volume will increase, at first slowly and then more and more rapidly. This means that the increase of velocity in a gas nozzle is relatively much more rapid than in the flow of an incompressible liquid and suggests the feasibility of applying Eq. (11:2), as follows:

$$\bar{V}_2 = \left\{ 2g \frac{k}{k-1} RT_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{(k-1)/k} \right] \right\}^{\frac{1}{2}} = 223.8 [c_p(T_1 - T_2)_s]^{\frac{1}{2}} \quad (11:7)$$

In the flow of a gas through a nozzle, the velocity and the specific volume increase as the pressure decreases in the direction of flow. In applying Eq. (3:8) to determine the shape of the nozzle, let us consider two successive sections across the passage, *a* and *b*, as in Fig. 11:4; the direction of flow is as indicated, and *b* is the downstream section. Let the specific volume and velocity of the fluid at section *a* be denoted as *v* and  $\bar{V}$ ,

respectively, and the higher values of these properties at section  $b$  will be designated as  $v + dv$  and  $\bar{V} + d\bar{V}$ . Then, from Eq. (3:8),

$$\frac{A_b}{A_a} = \frac{v_b}{v_a} \frac{\bar{V}_a}{\bar{V}_b} = \frac{v + dv}{v} \frac{\bar{V}}{\bar{V} + d\bar{V}} = \frac{1 + dv/v}{1 + d\bar{V}/\bar{V}} \quad (11:8)$$

It is evident from Eq. (11:8) that if  $d\bar{V}/\bar{V}$  is larger than  $dv/v$  then  $A_b/A_a < 1$  and the downstream section will be smaller. This is the condition

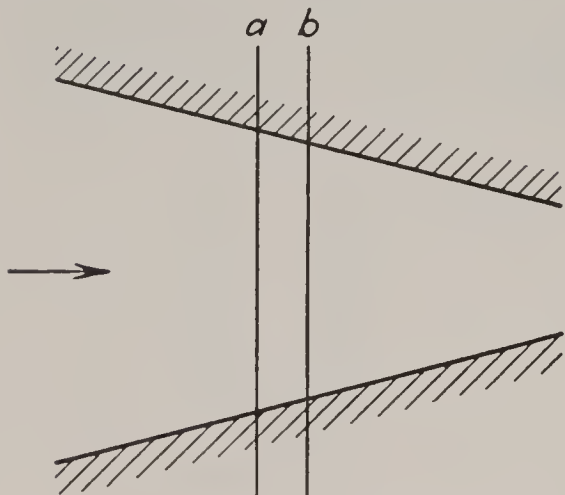


FIG. 11:4. Adjacent nozzle sections.

observed in the first section of a nozzle when the fluid enters at low velocity and indicates that this section of the nozzle should converge. As the pressure drops lower and lower, the rate of increase of specific volume becomes greater while the corresponding rate of increase of velocity becomes smaller; in later stages of the expansion,  $dv/v$  may therefore become larger than  $d\bar{V}/\bar{V}$ , and Eq. (11:8) indicates that nozzle areas must increase in the direction of flow. When  $dv/v = d\bar{V}/\bar{V}$ , the

nozzle will have reached its smallest area, or *throat*. Note that this will be the throat of a *nozzle* rather than a venturi, since the pressure will continue to decrease in the diverging section, although the passage may resemble a venturi in appearance.

The state of the fluid reached at the throat of a reversible adiabatic perfect-gas nozzle may be investigated by applying the equality  $dv/v = d\bar{V}/\bar{V}$ . For the isentropic process, we may write

$$Pv^k = P_1v_1^k \quad \text{or} \quad v = P_1^{1/k}v_1P^{-1/k} \quad \text{and} \quad dv = \frac{-1}{k} P_1^{1/k}v_1P^{-(k+1)/k} dP$$

$$\frac{dv}{v} = \left( \frac{-1}{k} P_1^{1/k}v_1P^{-(k+1)/k} \right) (P_1^{-1/k}v_1^{-1}P^{1/k}) dP = \frac{-dP}{kP} \quad (11:9)$$

Applying Eq. (11:7) to a section of the channel where the pressure is  $P$ ,

$$\begin{aligned} \bar{V}^2 &= 2g \frac{k}{k-1} RT_1 \left[ 1 - \left( \frac{P}{P_1} \right)^{(k-1)/k} \right] = 2g \frac{k}{k-1} P_1v_1 \left[ 1 - \left( \frac{P}{P_1} \right)^{(k-1)/k} \right] \\ &= 2g \frac{k}{k-1} P_1v_1 - 2g \frac{k}{k-1} P_1^{1/k}v_1P^{(k-1)/k} \\ \frac{d\bar{V}}{\bar{V}} &= \frac{2\bar{V} d\bar{V}}{2\bar{V}^2} = \frac{-2gP_1^{1/k}v_1P^{-1/k} dP}{4g \frac{k}{k-1} P_1v_1 \left[ 1 - \left( \frac{P}{P_1} \right)^{(k-1)/k} \right]} \\ &= \frac{-P^{-1/k} dP}{2 \frac{k}{k-1} [P_1^{(k-1)/k} - P^{(k-1)/k}]} \quad (11:10) \end{aligned}$$



At the throat,  $dv/v = d\bar{V}/\bar{V}$ . Designating the pressure at the throat as  $P_0$ ,

$$-\frac{dP}{kP_0} = \frac{-P_0^{-1/k} dP}{2 \frac{k}{k-1} P_1^{(k-1)/k} - 2 \frac{k}{k-1} P_0^{(k-1)/k}} \quad [\text{Eqs. (11:9) and (11:10)}]$$

from which

$$kP_0^{(k-1)/k} = 2 \frac{k}{k-1} P_1^{(k-1)/k} - 2 \frac{k}{k-1} P_0^{(k-1)/k}$$

or

$$\begin{aligned} \left(k + 2 \frac{k}{k-1}\right) P_0^{(k-1)/k} &= 2 \frac{k}{k-1} P_1^{(k-1)/k} \\ \left(\frac{P_0}{P_1}\right)^{(k-1)/k} &= \frac{2k/(k-1)}{k(k+1)/(k-1)} = \frac{2}{k+1} \end{aligned}$$

and

$$\frac{P_0}{P_1} = \left(\frac{2}{k+1}\right)^{k/(k-1)} \quad (11:11)$$

If the value of  $k$  for the monatomic gas (1.67) is substituted in Eq. (11:11), the ratio of throat to initial pressure will be found to be about 0.49. For air and the diatomic gases, the ratio is 0.53. For more complicated molecules, higher ratios will result. This ratio is called the *critical-pressure ratio* for gas flow.

In the flow of a gas through a converging nozzle such as that of Fig. 11:2, the pressure at the smallest section of the channel will be equal to the pressure on the exhaust side of the nozzle (the final pressure,  $p_2$ ) if that pressure is higher than the critical throat pressure, as calculated by applying Eq. (11:11). In that case, this section of smallest area would be the last section that would play any part in the expansion of the fluid and would therefore be the exit section. Accordingly, as illustrated in Fig. 11:5a, conditions at that point are designated by the subscript 2. If the nozzle is circular in cross section, the jet will issue from the nozzle in cylindrical form, as shown. If, as in sketch *b* of the figure, the exit pressure  $p_2$  is equal to the critical throat pressure, the flow will again issue in the form of a cylinder from the smallest section of the nozzle. This section may now, however, be properly called the throat, and the subscript 0 can be used to designate conditions at that point. The mass rate of flow will be somewhat greater than for case *a* because of the larger drop in pressure and temperature. Lastly, as the exhaust pressure becomes less than the critical throat pressure, the pressure *at the throat* will remain constant at  $p_0$ , the pressure drop from  $p_0$  to  $p_2$  taking place after the nozzle exit has been passed. In this part of the expansion,  $dv/v > d\bar{V}/\bar{V}$ , and the jet

expands in the exhaust space, as shown in Fig. 11:5c. The mass rate of flow will be determined by the flow through the smallest section and therefore by the drop in pressure and temperature between the entrance and this section. As the final pressure  $p_2$  decreases, the pressure at the

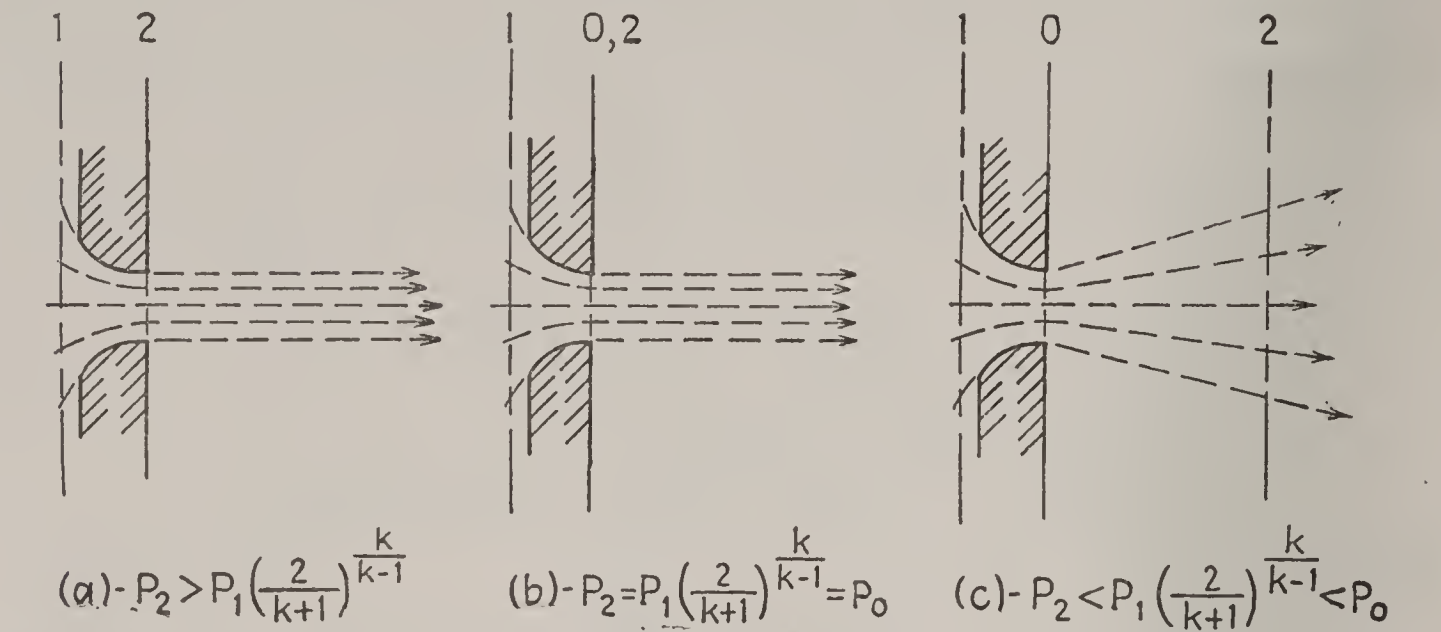


FIG. 11:5. Flow through a converging nozzle for various values of the ratio  $P_2/P_1$ .

smallest section will decrease with it until  $p_2$  equals  $p_0$ , the critical throat pressure. Any further decrease of  $p_2$  will not change the pressure at the throat, and consequently the mass rate of flow through the nozzle will

reach a maximum as  $p_2$  becomes equal to  $p_0$  and will thereafter remain constant at this maximum for any further decrease of the exhaust pressure. When  $p_2 < p_0$ , the nozzle is called an *expanding nozzle*. To reduce frictional effects in real flow, expanding nozzles should be designed with walls that continue beyond the throat section, diverging until the exit area is sufficient to meet the requirements of the flowing jet as it reaches the final pressure  $p_2$ .

In Fig. 11:6 is shown a converging-diverging nozzle. Also, this nozzle is acting as an expanding nozzle, as is indicated by the increase in  $v$  and  $\bar{V}$  beyond the throat in the chart at the lower part of the figure. These increases could have resulted only from a decreasing pressure in the diverging section

of the nozzle, and therefore the channel is not a venturi, for the venturi always includes a diffuser, with rising pressure in the direction of fluid flow. Yet the same channel may become a venturi under certain con-

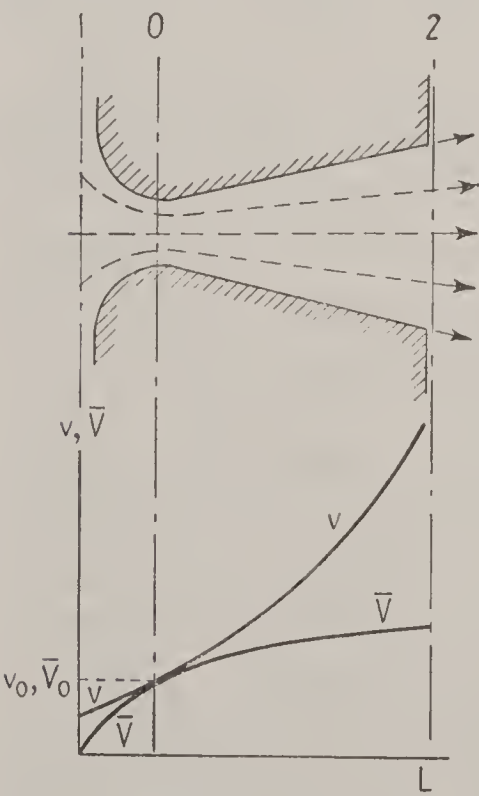


FIG. 11:6. The expanding nozzle.



ditions, as when  $p_2$  is equal to or greater than the critical throat pressure in gas flow or when the flowing fluid is an incompressible liquid.

The chart of Fig. 11:6 plots the specific volume and velocity of the gas against the distance traveled along the nozzle axis. Examination of the equation that connects the pressure and specific volume during an isentropic expansion will indicate that the specific volume will increase, at first slowly and then more and more rapidly, with respect to a unit decrease in pressure. The velocity, starting from practically zero, will increase at first very rapidly and later at a decreasing rate with respect to a unit pressure drop, as the fluid passes through the nozzle; this may be confirmed by returning to Eq. (11:7). If the scales to which  $v$  and  $\bar{V}$  are measured on the graph are adjusted to values such that the same distance measures both  $v_0$  and  $\bar{V}_0$ , the two curves will be tangent at the throat of the nozzle, as shown in Fig. 11:6.

The velocity at the throat of a gas nozzle may be calculated from Eqs. (11:7) and Eq. (11:11), as follows:

$$\bar{V}_0^2 = 2g \frac{k}{k-1} RT_1 \left[ 1 - \left( \frac{P_0}{P_1} \right)^{(k-1)/k} \right] = 2g \frac{k}{k-1} RT_1 \left( 1 - \frac{T_0}{T_1} \right) \quad [\text{Eq. (9:40)}]$$

$$\frac{T_0}{T_1} = \left( \frac{P_0}{P_1} \right)^{\frac{k-1}{k}} = \left( \frac{2}{k+1} \right)^{\frac{k}{k-1} \frac{k-1}{k}} = \frac{2}{k+1}$$

Also,

$$RT_0 = P_0 v_0$$

and, substituting in the equation for  $\bar{V}_0^2$  above,

$$\bar{V}_0^2 = 2g \frac{k}{k-1} P_0 v_0 \frac{k+1}{2} \left( 1 - \frac{2}{k+1} \right) = 2g \frac{k}{k-1} P_0 v_0 \frac{k+1}{2} \frac{k-1}{k+1} = kgP_0 v_0$$

or

$$\bar{V}_0 = (kgP_0 v_0)^{\frac{1}{2}} \quad (11:12)$$

Referring to texts in the field of physics, it is found that this expression is given as the velocity of sound in a gas at the pressure  $P_0$  and having the specific volume  $v_0$ . Thus the velocity attained at the throat in isentropic flow through an expanding nozzle is the velocity of sound in that gas under the conditions which exist at that point; this is the maximum velocity which can be reached in the converging section of a nozzle. The velocity downstream from the throat exceeds  $\bar{V}_0$  and is greater than the velocity of sound for the expanding isentropic nozzle.

If a gas, already traveling at a velocity in excess of the velocity of sound in that gas, enters a converging passage, its pressure will rise and its

velocity decrease in isentropic flow and the passage will act as a diffuser. From the point where, because of this diffuser effect, the velocity drops to the velocity of sound, the passage must diverge if the action is to continue to be that of a diffuser and to further build up the pressure and reduce the velocity. Thus the converging-diverging nozzle of Fig. 11:6 may become a diffuser over its entire length, and the implications of reversibility are emphasized. Conversely, if the flowing gas is to expand to lower pressures and is already traveling at the velocity of sound or above, a diverging passage must be provided.

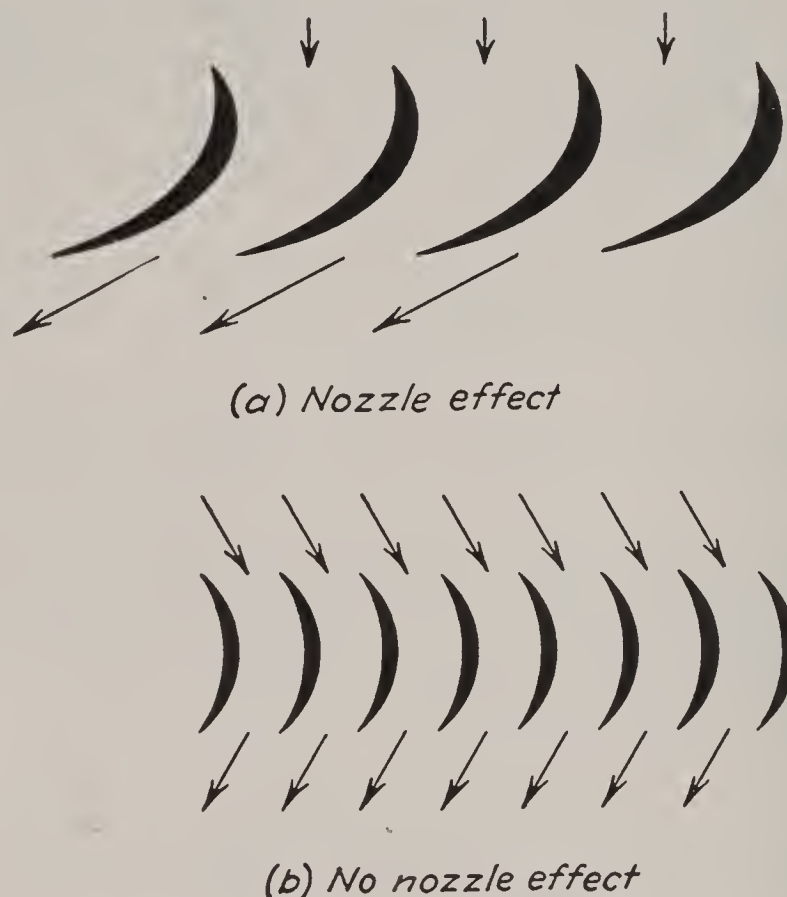


FIG. 11:7. Flow through turbine blading.

Nozzles need not, of course, be circular in cross section. The effect of a converging nozzle is often secured, in turbine design, by causing the fluid to flow through restricted passages between blades, or *vanes*, as shown in Fig. 11:7a. Here the exit area is less than that at entrance, and the fluid (traveling at a velocity less than that of sound) will leave it at increased velocity. When the purpose is merely to change the direction of flow without giving the effect of a nozzle, blades shaped as in Fig. 11:7b are used.

**Example 11:4.** What areas at the throat and exit of an air nozzle are required for the expansion of 3600 lb/hr from a pressure of 100 psia, temperature of 300°F, to a final pressure of 14.7 psia? Assume frictionless flow.

*Solution:*

$$\frac{p_0}{p_1} = \left( \frac{2}{k+1} \right)^{k/(k-1)} = \left( \frac{2}{2.4} \right)^{1.4/0.4} = 0.528 \text{ or } p_0 = 52.8 \text{ psia}$$

$$T_0 = T_1 \left( \frac{p_0}{p_1} \right)^{(k-1)/k} = (760)(0.528)^{0.4/1.4} = 633^\circ\text{R}$$



$$T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{(k-1)/k} = 760 \left( \frac{14.7}{100} \right)^{0.4/1.4} = 388^\circ\text{R}$$

$$\bar{V}_0 = 223.8[c_p(T_1 - T_0)]^{\frac{1}{2}} = 223.8[0.24(760 - 633)]^{\frac{1}{2}} = 1235 \text{ fps}$$

$$\bar{V}_2 = 223.8[0.24(760 - 388)]^{\frac{1}{2}} = 2110 \text{ fps}$$

$$v_0 = \frac{RT_0}{P_0} = \frac{(53.3)(633)}{(52.8)(144)} = 4.44 \text{ ft}^3/\text{lb}$$

$$v_2 = \frac{RT_2}{P_2} = \frac{(53.3)(388)}{(14.7)(144)} = 9.78 \text{ ft}^3/\text{lb}$$

$$A_0 = \frac{Mv_0}{\bar{V}_0} = \frac{(3600)(4.44)}{(60)(60)(1235)} = 0.0036 \text{ ft}^2 = 0.518 \text{ in.}^2 \text{ at throat}$$

$$A_2 = \frac{Mv_2}{\bar{V}_2} = \frac{(3600)(9.78)}{(60)(60)(2110)} = 0.00463 \text{ ft}^2 = 0.668 \text{ in.}^2 \text{ at exit.}$$

**11:5. The Vapor Nozzle.** The principles that govern the reversible flow of vapors are the same as for the flow of a perfect gas, with the exception that the perfect-gas relation cannot be employed and we must turn to tables and charts connecting the properties of the particular vapor in order to design a suitable nozzle for its expansion. For that purpose, Eqs. (11:1) and (11:2) will be found useful if the flow is isentropic, and Eq. (11:3) will also apply. Expansion to a certain critical-pressure ratio will, as for gas flow, be accompanied by the attainment of velocities equal to the velocity of sound in the vapor and by maximum flow rates for a given initial state. To expand to pressures less than this critical throat pressure requires a diverging nozzle passage, so that a throat is as characteristic of the expanding vapor nozzle as it is for the expanding perfect-gas nozzle.

The mass rate of flow through vapor nozzles is evidently again dependent upon the area of the smallest section. For maximum flow,  $dv/v_0 = d\bar{V}/\bar{V}_0$  at this point, as before. Equation (11:11) cannot, in strict accuracy, be applied to find the critical-pressure ratio  $p_0/p_1$ , since the derivation of that equation was based on the perfect-gas relation. But the isentropic process may be followed for the vapor, and, by trial and error, the critical pressure for a given expansion may be determined as the pressure reached when  $dv/v = d\bar{V}/\bar{V}$ . The ratio of this pressure to the assumed initial pressure gives the critical-pressure ratio for this expansion. A large number of such calculations are, of course, necessary before any conclusions may be drawn as to a general value of the ratio. However, experience has shown that Eq. (11:11) will hold very closely for the vapor, although  $k$  for the vapor is no longer the ratio of the specific heats, as for a gas. To avoid confusion, we shall designate it as  $n$ . In determining the value of  $n$  for use in this equation as it applies to the vapor, the pressures and volumes at two states having the same entropy may be determined and the relation  $P_1v_1^n = P_2v_2^n$  written, as for the perfect gas; from this relation,  $n$  may be computed. For superheated steam, the value of  $n$ , determined in this manner, quite uniformly approximates 1.31, and, for

saturated steam, the corresponding value is 1.13. When these values are substituted in Eq. (11:11), the corresponding critical-pressure ratios are

For steam initially superheated,

$$\frac{p_0}{p_1} = 0.55$$

For steam initially saturated,

$$\frac{p_0}{p_1} = 0.58$$

The Mollier chart will be found useful in the design of the vapor nozzle. The state of the vapor at entry to the nozzle is located as point 1 of Fig.

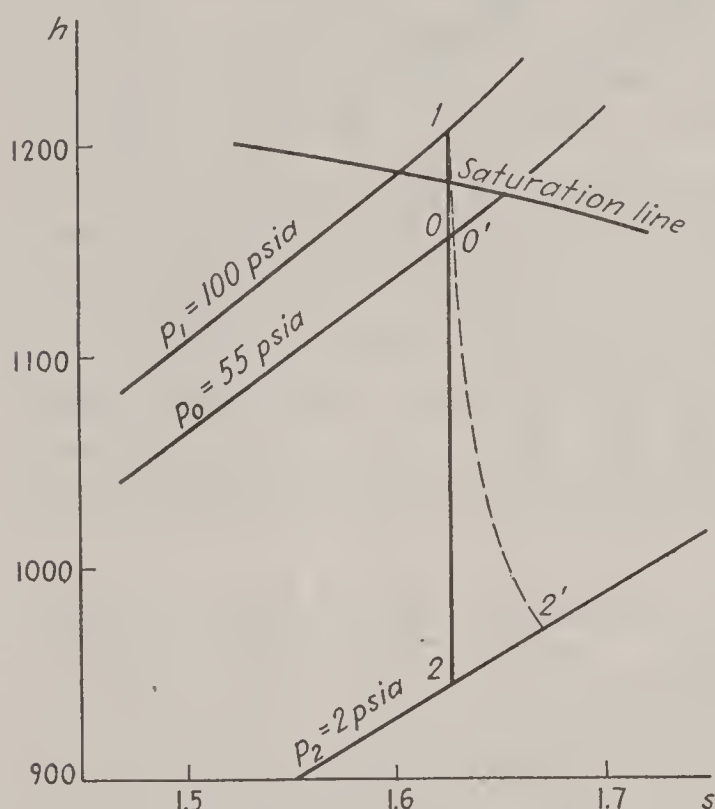


FIG. 11:8. Design of expanding vapor nozzle (data of Examples 11:5 and 11:6).

11:8. The expansion in the reversible adiabatic nozzle is isentropic, and a vertical line ( $ds = 0$ ) through point 1 cuts the exhaust pressure at point 2, locating the state of the vapor at exit. From the data thus obtained, the velocity of the vapor at exit from the nozzle and the required area of the nozzle at that point for a desired mass rate of flow may be calculated. For an expanding nozzle, such as is shown in the figure, the required throat area must also be determined. The condition at the throat is located as the intersection of the vertical line previously drawn with the constant-pressure line representing the critical throat pressure. If the vapor is steam and the state at entrance is in the superheat region, as illustrated in Fig. 11:8, this critical throat pressure  $p_0$  equals  $0.55p_1$ ; if the steam is initially saturated,  $p_0$  is  $0.58p_1$ . Other ratios would, of course, apply to other vapors and could be determined by applying the methods discussed in the earlier part of this article. When the point 0 has been located in the manner described above, the properties of the fluid at the throat are available and  $\bar{V}_0$  and  $A_0$ , the throat velocity and throat area for the required rate of flow, may be successively calculated.

The dashed line of Fig. 11:8 represents the effects of friction in the real nozzle and will be discussed later. It will be noted that, in accordance with the principle brought out in Chap. 6, the *nozzle condition line* 1-0'-2'



moves toward increasing entropies in reflecting the effects of irreversibility. The shape of the real nozzle expresses the designer's ideas and information as to the form that will give minimum friction in flow; simplicity and economy of the manufacturing process must also be considered. Between entrance and throat, a gradual convergence is the custom, resulting in a well-rounded entry section like that of the converging nozzle of Fig. 11:2. Between throat and exit, the walls are often conical in shape. When the nozzle is not an expanding nozzle (when the ratio  $p_2/p_1$  is greater than the critical-pressure ratio), the required effect may be obtained by the use of vanes shaped as in Fig. 11:7a.

*Example 11:5.* Find the required throat and exit areas for a nozzle to expand 3600 lb of steam per hour from 100 psia, 360°F, to a final pressure of 2 psia. Assume frictionless flow.

*Solution.* The steam is initially superheated, and therefore  $p_0 = (0.55)(100) = 55$  psia. The Mollier chart is used to obtain the data in the first three columns of the table below; in obtaining the tabulated data, the initial state is projected vertically (at constant entropy) to cut the lines of throat and exit pressures, and the data are read at the points of intersection. If the intersection is in the superheat region, the temperature is recorded in the third column; if below the saturation line, the quality is set down.

Section	$p$	$h$	$t$ or $x$	$\bar{V}$	$v$	$A$
Entrance	100	1206	360°F			
Throat	55	1156	0.979	1580	7.61	0.695
Exit	2	944	0.832	3610	144.5	5.76

The values tabulated in the last three columns of the table are calculated, as below:

$\bar{V}_0 = 223.8(h_1 - h_0)^{\frac{1}{2}} = 223.8(1206 - 1156)^{\frac{1}{2}} = 1580 \text{ fps}$

$\bar{V}_2 = 223.8(h_1 - h_2)^{\frac{1}{2}} = 223.8(1206 - 944)^{\frac{1}{2}} = 3610 \text{ fps}$

$v_0 = x_0 v_{g0} = (0.979)(7.787) = 7.62 \text{ ft}^3/\text{lb}$

$v_2 = x_2 v_{g2} = (0.832)(173.73) = 144.5 \text{ ft}^3/\text{lb}$

$A_0 = \frac{Mv_0}{\bar{V}_0} = \frac{(3600)(7.62)}{(60)(60)(1580)} = 0.00482 \text{ ft}^2 = 0.695 \text{ in.}^2$

$A_2 = \frac{Mv_2}{\bar{V}_2} = \frac{(3600)(144.5)}{(60)(60)(3610)} = 0.040 \text{ ft}^2 = 5.76 \text{ in.}^2$

In this example, the steam was wet steam at both throat and exit, and the condition was tabulated in terms of the quality. If it had been superheated at one or both of these points, the temperature would have been tabulated and the specific volume obtained from Table 3 of the steam tables, by interpolation if necessary.

**11:6. The Real Nozzle.** The effects of irreversibility in flow through the real nozzle, whether it be designed to expand a liquid, a gas, or a vapor, are expressed in terms of the *coefficient of velocity*, *coefficient of discharge*,

and the *nozzle efficiency*. The nozzle condition line bends to increasing entropies at lower pressures, in accordance with the principles outlined in Chap. 6, and follows a curve like 1-0'-2' of Fig. 11:8.

*Nozzle efficiency* is defined as the ratio of the kinetic energy of the stream as it leaves the real nozzle to that developable at exit from a reversible adiabatic nozzle which accepts the fluid at the same initial state (including the initial, or approach, velocity as one of the properties defining that state) and exhausts to the same final pressure. This ideal kinetic energy may be computed from Eq. (11:1) and is

$$\frac{\bar{V}_i^2}{2g} = \frac{\bar{V}_a^2}{2g} + J \Delta h_{sn} \quad (11:13)$$

where  $\bar{V}_i$ , the ideal velocity at exit, corresponds to  $\bar{V}_2$  for isentropic expansion,  $\bar{V}_a$  is the approach velocity [corresponding to  $\bar{V}_1$  in Eq. (11:1)], and the isentropic drop in specific enthalpy in the reversible nozzle [ $(h_1 - h_2)_s$  in Eq. (11:1)] is designated as  $\Delta h_{sn}$ . The efficiency may then be expressed as

$$\eta_n = \frac{\bar{V}_{2'}^2/2g}{\bar{V}_a^2/2g + J \Delta h_{sn}} \quad (11:14)$$

where  $\eta_n$  is the nozzle efficiency, a decimal fraction, and  $\bar{V}_{2'}$  is the velocity at exit from the real nozzle. When the approach velocity is negligible,<sup>1</sup> its effect may be ignored and Eq. (11:14) simplified to the form

$$\eta_n = \frac{\bar{V}_{2'}^2/2g}{J \Delta h_{sn}} \quad (11:15)$$

Equation (3:5) applies to the irreversible as well as to the reversible flow process and, neglecting approach velocity in flow through the real nozzle, that equation shows that  $\bar{V}_{2'}^2/2g = J(h_1 - h_{2'})$  and

$$\eta_n = \frac{h_1 - h_{2'}}{\Delta h_{sn}} = \frac{h_1 - h_{2'}}{h_1 - h_2} \quad (11:16)$$

where the subscripts refer to the corresponding points in Fig. 11:8. The efficiency of a well-designed expanding nozzle may be expected to be in the neighborhood of 0.90. Frictional effects increase rapidly with the velocity of the fluid, and the efficiency of the nonexpanding nozzle may be somewhat higher.

The *coefficient of velocity of a nozzle* is defined as the ratio of the velocity of the fluid as it leaves the real nozzle to its velocity as it leaves the ideal

<sup>1</sup> Calculation will show that it requires an approach velocity of about 224 fps to have the effect of adding 1 Btu to the isentropic enthalpy drop  $\Delta h_{sn}$  in the denominator of Eq. (11:14).



nozzle which operates under equivalent conditions. This ideal velocity is, from Eq. (11:1),

$$\bar{V}_i = (\bar{V}_a^2 + 2Jg \Delta h_{sn})^{\frac{1}{2}}$$

and

$$C_{v_n} = \frac{\bar{V}_{2'}}{(\bar{V}_a^2 + 2Jg \Delta h_{sn})^{\frac{1}{2}}} \quad (11:17)$$

where  $C_{v_n}$  is the nozzle coefficient of velocity, a decimal fraction. Neglecting the approach velocity, this becomes

$$C_{v_n} = \frac{V_{2'}}{(2Jg \Delta h_{sn})^{\frac{1}{2}}} \quad (11:18)$$

A comparison of Eq. (11:17) with Eq. (11:15) or of Eq. (11:18) with Eq. (11:16) will show, in either case, that

$$C_{v_n} = \eta_n^{\frac{1}{2}} \quad (11:19)$$

When the real nozzle is to be designed as an expanding nozzle, the throat area must be calculated to give the desired rate of flow. The velocities in the converging section of the nozzle are less than those after the throat is passed. This causes the effects of friction to be less in evidence at the throat than over the entire expansion, and the coefficient of velocity at the throat is higher than the coefficient of velocity of the nozzle. In fact, it is often assumed that all friction takes place between throat and exit of the expanding nozzle, and the entry section is designed as a reversible adiabatic nozzle. Based upon the value of the nozzle efficiency suggested above, it is evident that the coefficient of velocity to be expected in the well-designed expanding nozzle is about 0.95; it cannot, of course, exceed 1, since any value in excess of 1 would be a violation of Second Law principles. A reasonable value of the coefficient of velocity at the throat is about 0.99. Any value less than 1 at this location will mean that the velocity of sound will not be attained as the throat is passed in the real expanding nozzle and that this velocity will not be reached until at least some distance after the diverging section of the channel has been entered.

The *coefficient of discharge* compares the mass rate of fluid flow through the real nozzle with that through the same nozzle when the flow is isentropic and the same entry conditions and exhaust pressure apply. If the nozzle is nonexpanding, the theoretical rate will be based on the exit area of the nozzle and is  $M_i = A_2 \bar{V}_s / v_s$  or, neglecting approach velocity,

$$C_d = \frac{M}{M_i} = \frac{M v_s}{A_2 \bar{V}_i} = \frac{M v_{sn}}{223.8 A_2 (\Delta h_{sn})^{\frac{1}{2}}} \quad (11:20)$$

where  $C_d$  = discharge coefficient

$M$  = mass rate of flow through the real nozzle

$v_{sn}$  = specific volume of the fluid at the exhaust pressure and an entropy equal to that at entrance to the nozzle

$\bar{V}_s$  = ideal velocity, or velocity attained as the result of isentropic flow

If the nozzle is an expanding nozzle, the theoretical mass rate of flow will be based on the throat area  $A_0$  and

$$C_d = \frac{M v_{snt}}{223.8 A_0 (\Delta h_{snt})^{\frac{1}{2}}} \quad (11:21)$$

where  $v_{snt}$  is the specific volume at the critical throat pressure and an entropy equal to that at entrance to the nozzle and  $\Delta h_{snt}$  is the isentropic drop of enthalpy from entrance to throat of the reversible adiabatic nozzle.

Since the effect of friction is to slow down the fluid and to increase its specific volume above that which would result from frictionless flow (the entropy is higher than would result from isentropic flow, and this, at the same pressure, means greater volume), it would seem that the discharge coefficient, like the coefficient of velocity, could not exceed 1. This is not a requirement of the Second Law, however, and we shall shortly investigate flow situations that are accompanied by mass rates of flow higher than the theoretical.

*Example 11:6.* Assume conditions similar to those of Example 11:5 except that the flow is not reversible. The coefficient of velocity at the throat is assumed to be 0.99 and the nozzle efficiency (entrance to exit) as 0.90. Based upon the same rate of flow (3600 lb/hr), calculate the required areas at throat and exit, the discharge coefficient, and the velocity and velocity coefficient at the exit. Neglect approach velocity as in Example 11:5.

*Solution.* The velocity at the throat is  $(0.99)(1580) = 1564$  fps. This velocity is equivalent to an enthalpy drop from entrance to throat of  $1564^2/(64.4)(778) = 49$  Btu, and the enthalpy at the throat is therefore  $1206 - 49 = 1157$  Btu. When this enthalpy and the pressure of 55 psia are taken to the Mollier diagram, the quality at the throat is observed to be 0.98; the specific volume is  $(0.98)(7.787) = 7.63$  ft<sup>3</sup>/lb. Then  $A_0 = (3600)(7.63)/(60)(60)(1564) = 0.00487$  ft<sup>2</sup> = 0.702 in.<sup>2</sup> This is the area at the throat required to obtain the desired rate of flow. The coefficient of discharge for this expanding nozzle is based on Eq. (11:21),

$$C_d = \frac{M v_{st}}{A_0 (\Delta h_{snt})^{\frac{1}{2}}} = \frac{(3600)(7.62)}{(60)(60)(0.00487)(50)^{\frac{1}{2}}} = 0.99$$

The coefficient of discharge might also have been calculated as the ratio of the throat area required to obtain the desired rate of flow if frictionless to that area necessary under the assigned conditions, or  $0.00482/0.00487 = 0.99$ . It will be noted that, unless the effects of friction are unusually large, the discharge coefficient will be approximately equal to the velocity coefficient at the throat (or at the exit, if the nozzle is a converging nozzle).



The nozzle efficiency is 0.90. From Eq. (11:16),

$$0.90 = \frac{1206 - h_{2'}}{1206 - 944} \text{ or } h_{2'} = 970 \text{ Btu/lb}$$

This enthalpy and the final pressure of 2 psia make it possible to read the final quality from the chart, as  $x_{2'} = 0.856$ . The specific volume at exit is  $v_{2'} = (0.856)(173.73) = 148.5 \text{ ft}^3/\text{lb}$ . Also,

$$\bar{V}_2 = 223.8(1206 - 970)^{\frac{1}{2}} = 3430 \text{ fps}$$

$$A_2 = \frac{(3600)(148.5)}{(60)(60)(3430)} = 0.0433 \text{ ft}^2 = 6.24 \text{ in.}^2$$

$$C_{v_n} = \eta_n^{\frac{1}{2}} = 0.90^{\frac{1}{2}} = 0.949$$

Checking,

$$C_{v_n} = \frac{3430}{3600} = 0.95$$

**11:7. Pressure Variation in the Convergent-Divergent Nozzle.** Figure 11:9 is adapted<sup>1</sup> from a report of tests made on a convergent-divergent steam nozzle at various ratios of exhaust to supply pressure. It plots the

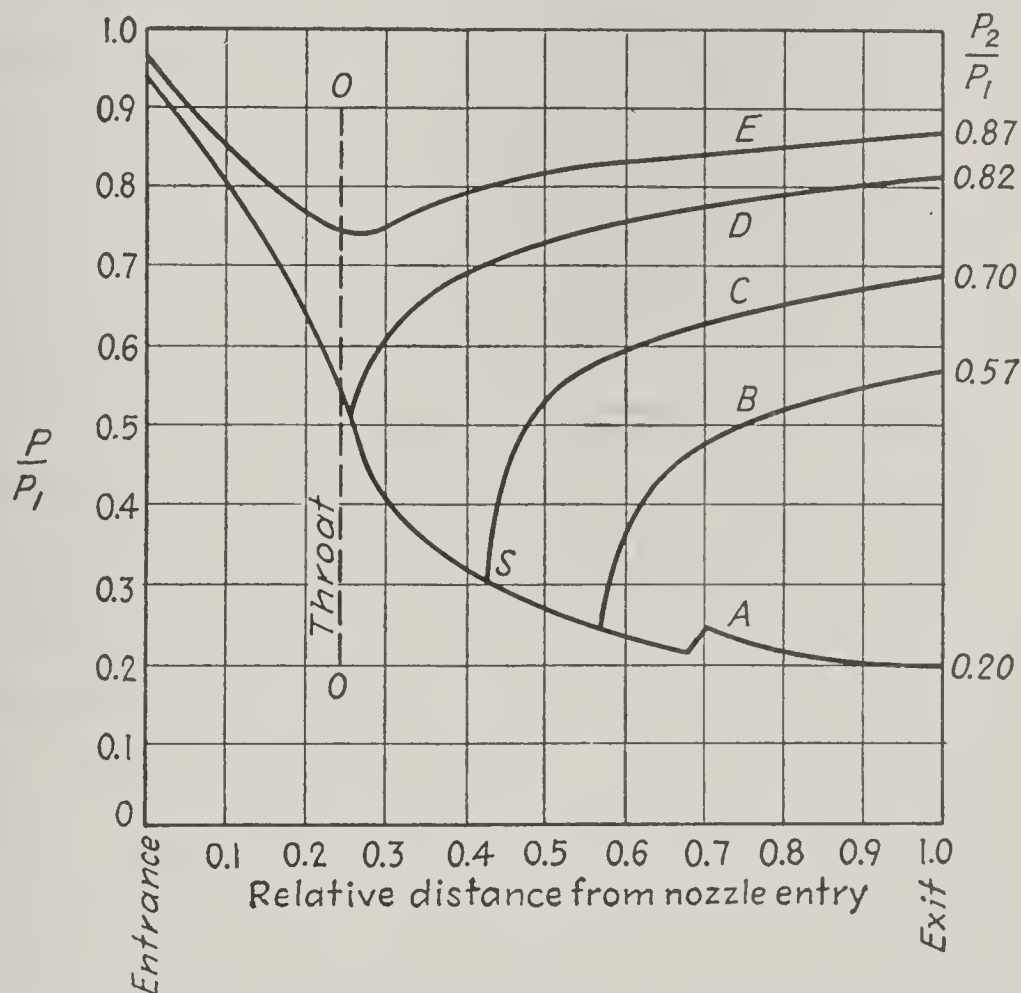


FIG. 11:9. Pressure variation in a convergent-divergent nozzle.

ratio of the pressure at successive stations along the length of the nozzle to the pressure at which superheated steam was supplied the nozzle, for various ratios of exhaust to initial pressure,  $p_2/p_1$ . These pressures were measured at a series of small holes in a tube which extended along the axis of the nozzle.

<sup>1</sup> From Binnie and Woods, *Proc. Inst. Mech. Engrs.*, **138** (1938).

The nozzle was apparently designed for a pressure ratio of expansion of about 0.2, and curve *A* of the figure shows the observed pressure variation under that condition. It will be noted that the pressure ratio at the throat agrees with the critical-pressure ratio for superheated steam. The small rise in pressure on curve *A* near the 0.7 station is the result of sudden condensation that is produced due to a flow condition to be discussed in later pages of this chapter; the pressure in the nozzle again decreases after this discontinuity has been passed. Curve *E* records the pressure variation in the same nozzle when the exhaust pressure is about 87 per cent of the supply pressure. For this case, the pressure at the throat, while above the critical throat pressure, is less than the exhaust pressure, and the diverging section of the channel acts as a diffuser. In calculating the discharge coefficient, the theoretical mass rate of flow would be based on the assumption that the pressure at the throat was the exhaust pressure, and it would therefore be possible for the discharge coefficient to be greater than 1. In curve *D*, where the ratio  $p_2/p_1$  is about 0.82, the same effect is observed, but in this case the throat pressure has declined to its critical, or minimum, value and the mass rate of flow through the nozzle is probably near the maximum. Although the pressure is still dropping at a point slightly beyond the throat, it is doubtful that the velocity of sound is attained, because of frictional effects. Curve *C*, with  $p_2/p_1$  equal to about 0.7, follows the pressure variation of curve *A* to a point well beyond the throat and then breaks sharply upward from this curve. The first sudden rise in pressure (denoted by *s* on the curve) is caused by a standing pressure wave in the nozzle which is called *pressure shock*. After passing this shock wave, the pressure rise becomes more gradual and more typical of diffuser action. To enter a shock wave of this kind, the fluid must have attained a velocity greater than the velocity of sound. Since the pressure is lower at this point than that at exit from the nozzle, the later sections of the nozzle must act as a diffuser. But these sections continue to diverge and can have a diffuser effect only if the velocity of the fluid is less than that of sound, as explained in Art. 11:4. The fluid enters the shock wave at a velocity higher than that of sound and leaves it at a velocity which has suddenly been reduced below that of sound; it is then in a condition such that it can utilize the diverging passage as a diffuser.

A more complete thermodynamic explanation of pressure shock will be reserved for a later chapter. It will be shown there that the flow through the shock is irreversible and always characterized by decreasing velocities and increasing pressures. Being irreversible, it causes a loss in nozzle efficiency and is therefore to be avoided in design. The effect on nozzle efficiency is most serious when the exhaust pressure is about midway between the exhaust pressure of curve *D*, where the throat pressure first reached its critical value, and that of curve *A*, for which the nozzle was designed.



**11:8. Metastable Expansion—Supersaturated Steam.** The preceding article has included an explanation of why the discharge coefficient of the converging-diverging nozzle may exceed 1. But even the converging nozzle may have discharge coefficients slightly greater than 1, and the conditions that make this possible are the subject of our present discussion.

In Fig. 11:8 is shown the change in state of the steam as it flows through a steam nozzle. If this were a converging nozzle, the expansion could proceed no further than point 0, but, for the case illustrated, where the steam enters the nozzle moderately superheated, the steam would have crossed the saturation line in the course of its expansion. If this expansion had taken place slowly, the crossing of the saturation line would have marked the condition at which the kinetic energy of the molecules is no longer sufficient to resist their mutual attraction for one another and small groups of molecules would have begun to form nuclei, about which still further condensation could proceed. But the expansion, as it proceeds in the nozzle, is exceedingly rapid and is accompanied by sweeping temperature changes. Here and there, molecules will form into small collections but, until the group reaches a certain critical size, will tend to again separate. This tendency toward reevaporation of the minute droplet is a result of the surface tension of the liquid in producing the effect of a taut, rubberlike skin over the surface of the droplet. The tension in this skin accounts, because of the small radius of curvature of the surface, for a disparity between the pressure of the liquid and of the vapor molecules, and the former find it easier to escape than do the latter to become a part of the group of liquid molecules. When the droplets reach a certain critical size, which is smaller for lower steam pressures and correspondingly higher specific volumes, this effect vanishes and condensation begins. Condensation, when it starts, is rapid, and a dense cloud of liquid particles makes its appearance suddenly at a point in the nozzle well beyond that at which condensation would have begun if stable equilibrium had been maintained. Yellott<sup>1</sup> observed this phenomenon through the glass walls of a specially prepared nozzle. The steam, between the point where it crosses the saturation line and that at which stable expansion is resumed with the sudden formation of the cloud of liquid droplets, is called *supersaturated steam*. Its temperature is less than the saturation temperature corresponding to its pressure. It is said to be in a state of *metastable equilibrium*, meaning that a disturbance of finite magnitude is required to restore it to completely stable equilibrium. It might be compared to the equilibrium of a ball resting in the bottom of a shallow depression at the top of a cone. For small disturbances, the ball is in stable equilibrium and will return to the bottom of its hollow; a disturbance sufficient to

<sup>1</sup> J. I. Yellott and C. K. Holland, "Condensation of Steam in Diverging Nozzles," *Trans. ASME*, **59**, (April, 1937).

move it over the rim of the depression will bring about a sweeping change. The necessary disturbance, in the case of supersaturated steam, is the formation of drops of the critical size. This may be the result either of the accidental accumulation of a sufficient number of molecules or of a continuation of the expansion to pressures low enough so that very small collections will suffice. At a pressure of 6 psia, a collection of about 12 molecules will form a drop of critical size and this group will have a radius of curvature of about  $1.4 \times 10^{-9}$  ft.

Yellott and Holland (see footnote, page 247) found that the limit of supersaturation in the flow of steam through a converging-diverging nozzle (the point at which the cloud of liquid particles was suddenly formed) was about 60 Btu below the saturation line on the Mollier diagram. If the steam has passed the throat of the nozzle in the form of supersaturated steam, conditions at the throat, including the mass rate of flow, will be affected. To investigate these conditions, it is customary to extrapolate the equilibrium relations for the superheated steam into the region below the saturation line. It will be remembered that  $n$  during isentropic expansion of superheated steam is about 1.31, for saturated steam around 1.13. When the two isentropic expansion curves,  $Pv^{1.31} = C$  and  $Pv^{1.13} = C$ , are compared on a  $PV$  diagram (see Fig. 9:3), it will be observed that the expansion as supersaturated steam will give greater densities at equal pressures. Neither the pressure nor the velocity at the throat will be greatly different for the two types of expansion. This means that a larger mass of supersaturated steam will pass the throat than would be possible if the steam were wet. Thus, discharge coefficients larger than 1 are possible if supersaturation is present at the throat of a nozzle. If the steam is highly superheated at entrance to the nozzle, the throat may be passed before the steam reaches the saturation line and becomes supersaturated; in this case, supersaturation could not account for flow rates above the theoretical.

The sudden accumulation of the cloud of liquid particles at the limit of supersaturation is accompanied by a small rise of pressure of the steam as the steam adjusts to a state of stable equilibrium. It is this effect which accounts for the discontinuity in curve  $A$  of Fig. 11:9, to which attention was called in Art. 11:7.

*Example 11:8.* In Example 11:5, assume that the steam was supersaturated as it passed the throat of the nozzle. Calculate the coefficient of discharge.

*Solution.* The flow equations of a gas with  $n = 1.31$  are used to extrapolate the expansion of the steam as a dry vapor to throat pressure. The critical-pressure ratio

$$\frac{p_0}{p_1} = \left( \frac{2}{n+1} \right)^{n/(n-1)} = \left( \frac{2}{2.31} \right)^{1.31/0.31} = 0.542, \text{ or } p_0 = 54.2 \text{ psia}$$

Equation (11:7) may be used to calculate the velocity.



$$\begin{aligned}
 \bar{V}_0 &= \left\{ 2g \left( \frac{n}{n-1} \right) RT_1 \left[ 1 - \left( \frac{p_0}{p_1} \right)^{(n-1)/n} \right] \right\}^{\frac{1}{2}} \\
 &= \left\{ (64.4) \left( \frac{1.31}{0.31} \right) (85.8)(820) [1 - (0.542)^{0.31/1.31}] \right\}^{\frac{1}{2}} \\
 &= 1605 \text{ fps} \\
 v_0 &= v_1 \left( \frac{p_1}{p_0} \right)^{1/n} = 4.663 \left( \frac{1}{0.542} \right)^{1/1.31} = 7.43 \text{ ft}^3/\text{lb} \\
 M &= \frac{A_0 \bar{V}_0}{v_0} = \frac{(0.00482)(1605)}{7.43} = 1.04 \text{ lb/sec, or } 3744 \text{ lb/hr}
 \end{aligned}$$

This corresponds to a discharge coefficient of  $\frac{3744}{3600} = 1.04$ .

**11:9. Turbine Staging.** Steam may be supplied to the modern central-station turbine prime mover at pressures above 1000 psia, and the exhaust pressure may be less than 1 psia. When these pressures are taken to a Mollier diagram for steam, it is found that the isentropic drop in specific enthalpy would approach 600 Btu, and if the expansion were carried out in a single bank of nozzles, the theoretical velocity reached by the steam would be some 5500 fps. The losses caused by flow friction increase rapidly with the velocity after the velocity of sound (about 1500 to 1700 fps) is passed, as has been brought out in earlier pages of this chapter, and even if the reduction of irreversibility due to friction were the only gain to be expected, the division of the total drop of pressure and enthalpy into steps, by the use of banks of nozzles in series, would have an advantage which could not be ignored. But there are other benefits, several of which will develop in the course of the discussion to follow. For example, if the expansion is staged, it will be possible to withdraw part or all of the steam at pressures intermediate between the pressures of supply and of exhaust, should that be desirable for any reason.

If the total enthalpy drop through the turbine is divided into steps of 50 Btu or less, the maximum velocity reached by the steam will be less than the acoustic velocity and converging nozzles may be used. The effect of a converging nozzle may be attained by the use of the blade arrangement illustrated in Fig. 11:7*a*; nozzles so formed have the advantage of economy in their cost and their space requirements.

If the series of pressure drops occur only in stationary nozzles, with no essential drop in pressure through the moving buckets, the staging is of the *impulse* type; if, on the other hand, these pressure drops take place in both stationary and moving blades, the resulting arrangement is called *reaction staging*. A *pure impulse* or a *pure reaction* stage is an idealization never found in the real turbine; all real turbine stages have some of the elements of impulse and some of the characteristics of reaction design. For example, blades of the type sketched in Fig. 11:7*b* are used as the buckets in the impulse stage; because of fluid friction, the velocity at exit tends to be less than at entrance, but this is impossible, according to the

continuity equation, since the area at exit is no larger than that at entrance. The pressure must therefore drop at least slightly across these moving buckets, and this means a corresponding increase of specific volume of the fluid and, according to Eq. (3:8), an increased velocity at exit. It is evident that this requirement of increased velocity has the effect of still further increasing the pressure drop across the bucket. The staging of the real turbine is classified as impulse or reaction according to the characteristics which predominate in its design. The same turbine may utilize impulse stages over a part of its over-all pressure and enthalpy drop and reaction staging for the balance, depending upon the relative advantages of each in high- and low-pressure ranges. It is not appropriate to the purposes of this text to go into the details of turbine design, and we shall content ourselves with an examination of the basic types of staging and their general characteristics from the thermodynamic viewpoint.

**11:10. Impulse Staging.** A series of four impulse stages is diagramed in Fig. 11:10; the pattern of the pressure, enthalpy, and velocity changes of the fluid as it moves through these stages is charted below. It is here assumed that the bucket velocity is the same in each stage; this would be the case, for example, if the blade-circle diameter (the diameter of a circle cutting the mid-height of each blade in a ring of blades) of each row of moving buckets was the same and the disks, or rotors, on which these buckets are mounted, were keyed to the same shaft. Each stage begins at the entrance to a row of stationary nozzles and ends when the fluid is ready to enter the next row of nozzles. The enthalpy drop is the same for each stage, and, assuming the flow through the buckets to be frictionless, this drop is effected entirely in the stationary nozzles. To obtain these equal enthalpy drops, the pressure drops through the high-pressure stages must be greater than through succeeding stages; there is no pressure drop across the buckets for frictionless flow. The absolute velocity (the velocity relative to the stationary nozzles) of the fluid reaches a maximum at exit from each row of nozzles and a minimum at exit from the moving buckets of each stage; the maxima and minima are the same for each stage under the conditions we have assumed. Because the mass rate of flow through each stage is the same, as is the kinetic energy of the fluid at entrance to and exit from each row of moving blades, each stage develops the same power.

Some features of the design of the impulse turbine are immediately apparent. Since there is only a very small drop in pressure across the moving buckets (zero drop for the reversible case illustrated), leakage over the top of these blades is negligible and it is unnecessary to provide close clearances between them and the turbine casing. At a given instant, work is performed on those buckets which are directly in the path of the jet as it issues from the stationary nozzles; the rest of the buckets are idle.



In the lower pressure stages, the specific volume of the fluid is greater, and larger passages must be provided for flow through both nozzles and moving buckets. This increased area is provided both by increasing the height of both moving and stationary blades and by increasing the proportionate number of moving buckets that are in action at one time; in the first few stages the nozzles cover only a portion of the periphery.

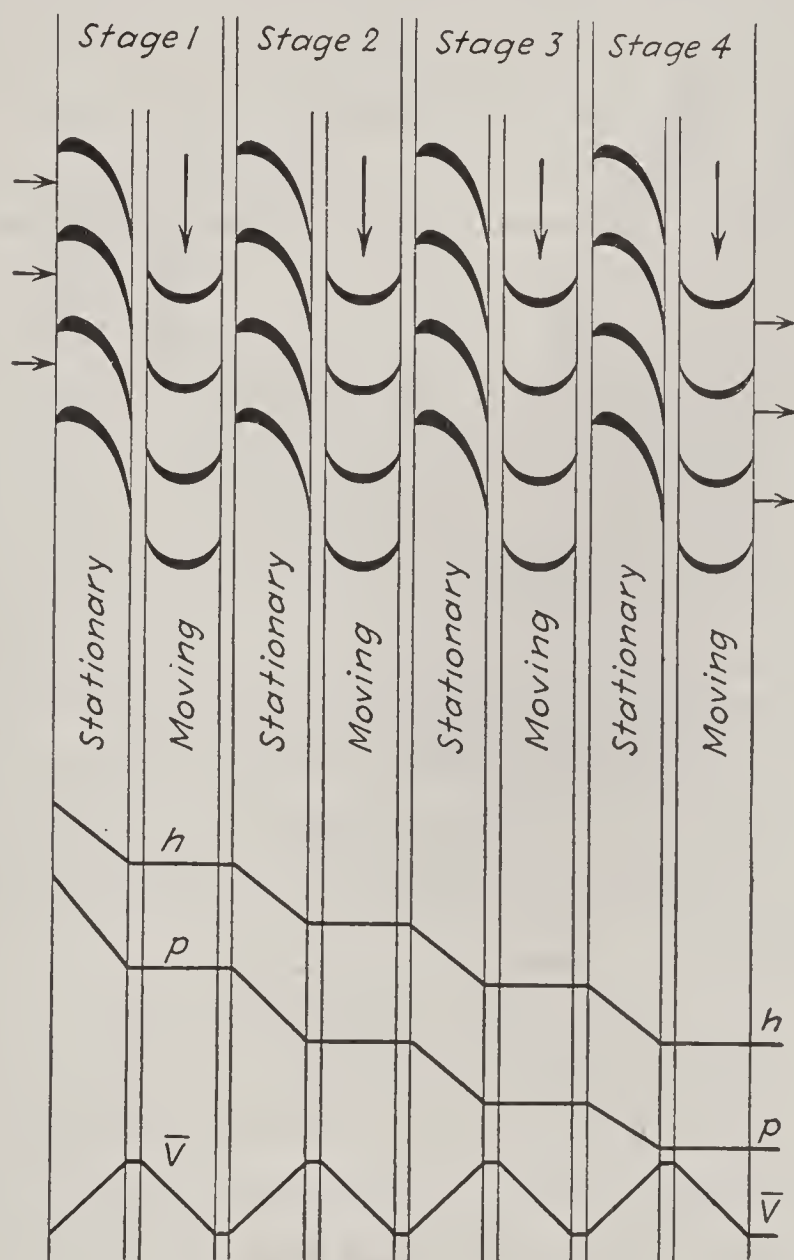


FIG. 11:10. Enthalpy, pressure, and velocity variation through an impulse turbine.

In Fig. 11:11 is shown a vector diagram of the velocities through one of the stages of Fig. 11:10; the vector diagram for all of its stages will be the same under the assumptions made. In the construction of Fig. 11:11, it is assumed that the flow through the moving bucket is reversible (frictionless) so that the velocity  $\bar{V}_2$ , relative to the bucket at entrance, is equal to the velocity  $\bar{V}_3$ , relative to the same bucket at exit. The bucket entrance and exit angles  $\beta_1$  and  $\beta_2$  are equal. The absolute velocity of the fluid at exit from the stationary nozzle is designated as  $\bar{V}_1$ , and this vector makes an angle  $\alpha$  (the *nozzle angle*) to the plane of rotation of the bucket. The absolute velocity of the bucket is indicated as  $\bar{V}_b$ , and the final (absolute) exit velocity from the stage is  $\bar{V}_4$ . The vectorial subtraction of  $\bar{V}_b$

from  $\bar{V}_1$  gives  $\bar{V}_2$ . The entry angle of the bucket is such that the jet may enter tangentially to the surface of the bucket on which it is to act, and  $\beta_1$  is therefore established from the direction of  $\bar{V}_2$ . When friction is ignored and the velocity relative to the bucket is the same in magnitude at exit as at entrance,  $\beta_2$ , the exit angle of the bucket is made equal to  $\beta_1$ , as in the diagram. The vectorial addition of  $\bar{V}_b$  and  $\bar{V}_3$  gives the absolute exit velocity  $\bar{V}_4$ .

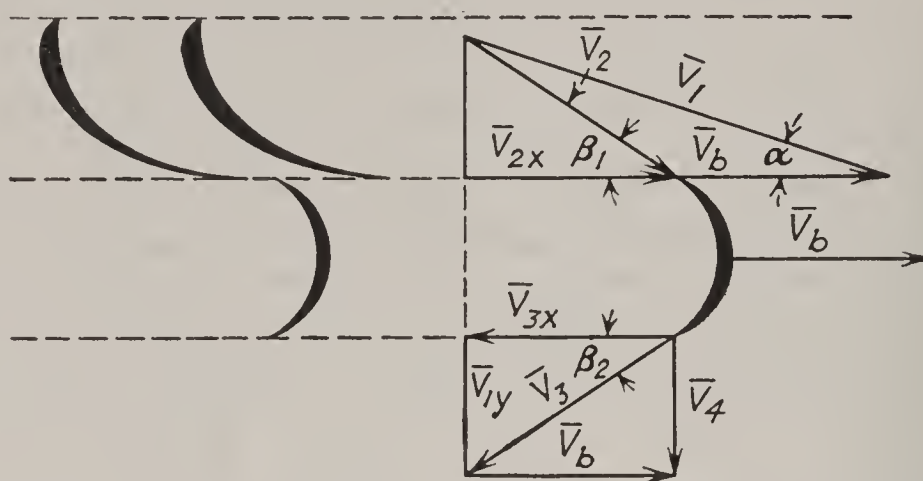


FIG. 11:11. Velocity diagram—impulse stage (maximum work).

It is convenient to resolve the various velocities into their components parallel and perpendicular to the plane of bucket rotation. The parallel component will be designated by the subscript  $x$ , and the perpendicular component by  $y$ ; thus  $\bar{V}_{1x} = \bar{V}_1 \cos \alpha$  and  $\bar{V}_{1y} = \bar{V}_1 \sin \alpha$ . Referring to Fig. 11:11 and considering the direction of  $\bar{V}_b$  as positive, we may write the following relations:

$$\begin{aligned}\bar{V}_{2x} &= \bar{V}_{1x} - \bar{V}_b = \bar{V}_1 \cos \alpha - \bar{V}_b \\ \bar{V}_{3x} &= -\bar{V}_{2x} \\ \bar{V}_{4x} &= \bar{V}_{3x} + \bar{V}_b = -\bar{V}_1 \cos \alpha + 2\bar{V}_b\end{aligned}$$

The force on the bucket may be calculated as equal to the change of momentum of the fluid in the direction of bucket movement and the work per pound of fluid flow as the product of this force and  $\bar{V}_b$ . Thus

$$W \text{ per lb} = F\bar{V}_b = \frac{(\bar{V}_{2x} - \bar{V}_{3x})\bar{V}_b}{g} = \frac{2(\bar{V}_1 \cos \alpha - \bar{V}_b)\bar{V}_b}{g} \quad (11:22)$$

For maximum work,

$$\frac{dW}{d\bar{V}_b} = \frac{2}{g} (\bar{V}_1 \cos \alpha - 2\bar{V}_b) = 0 \quad \text{or} \quad \bar{V}_b = \frac{1}{2} \bar{V}_1 \cos \alpha \quad (11:23)$$

The maximum work is found by substitution of this value of  $\bar{V}_b$  in Eq. (11:22), or

$$W_{\max} \text{ per lb} = \frac{2}{g} \left( \bar{V}_1 \cos \alpha - \frac{1}{2} \bar{V}_1 \cos \alpha \right) \frac{1}{2} \bar{V}_1 \cos \alpha = \frac{\bar{V}_1^2}{2g} \cos^2 \alpha \quad (11:24)$$



It will be noted from Eq. (11:24) that, as the nozzle angle approaches zero, total conversion of the kinetic energy of the jet, as it leaves the stationary nozzles, into work on the impulse bucket is approached. However, the component of velocity normal to the plane of blade rotation must be large enough to clear the fluid, as it exits from the moving buckets, from the path of following buckets. Moreover, except in the final stage of expansion, this unremoved kinetic energy is not a thermodynamic loss, for it allows the fluid to enter the next row of nozzles with an approach velocity and is thus, in theory, completely recoverable in later expansion. Nozzle angles are normally around  $20^\circ$ .

Equation (11:22) indicates that the work output of the impulse stage and, indirectly, the turbine efficiency are quite sensitive to changes in rotative speed. For best results, the bucket speed should differ only negligibly from that expressed in Eq. (11:23). The impulse turbine is designed to operate at constant speed and is not suited to variable-speed operation. Equation (11:23) also brings out an additional advantage of multistaging. If the entire expansion were effected in a single row of nozzles, it has been shown in Art. 11:9 that the velocity  $\bar{V}_1$  might conceivably approach 5500 fps. The optimum bucket speed, which corresponds to this jet velocity and a nozzle angle of  $20^\circ$ , is about 2500 fps. For a rotor of 4 ft diameter, this corresponds to about 12,000 rpm. This would be an impossible speed from the standpoint of design because of the excessive centrifugal stresses which would be created in the rotor; moreover, the utilization of power delivered under this condition of extreme rotative speed would be difficult and would invite high losses due to mechanical friction and other factors.

A *two-row impulse stage* is diagramed in Fig. 11:12, and a vector diagram of this stage is presented in Fig. 11:13. Only a single row of stationary nozzles is used; the stationary vanes have the function of merely changing the direction of fluid flow. In the vector diagram, frictionless flow is assumed, and  $\bar{V}_2 = \bar{V}_3$ ,  $\bar{V}_4 = \bar{V}_5$ , and  $\bar{V}_6 = \bar{V}_7$  in magnitude, though not in direction. The blade angles are shown as equal at entrance to and exit from each row of blades, with the exception of the row of blades that forms the stationary nozzles, but these blades become shallower in the direction of flow. Approximately half the velocity of the jet is removed in the first row of buckets; thus the two-row impulse stage accounts for about three-fourths of its power output from the first row of moving buckets, one-fourth from the second. For a given bucket speed, jet velocities are higher for this two-row stage as compared with the single-row impulse stage discussed above, and frictional losses are correspondingly greater, but it has the virtue of permitting a larger drop of pressure and enthalpy per row of buckets at the expense of somewhat lowered efficiency. For the same blade speed, note that  $\bar{V}_1$  for the two-row stage is approximately

double  $\bar{V}_1$  for the single row; this is equivalent to an enthalpy drop four times as large. Therefore, based on the same bucket speed, the arrangement of Fig. 11:12 is capable of utilizing about the same enthalpy drop as the four impulse stages of Fig. 11:10. Three- and four-row stages are also

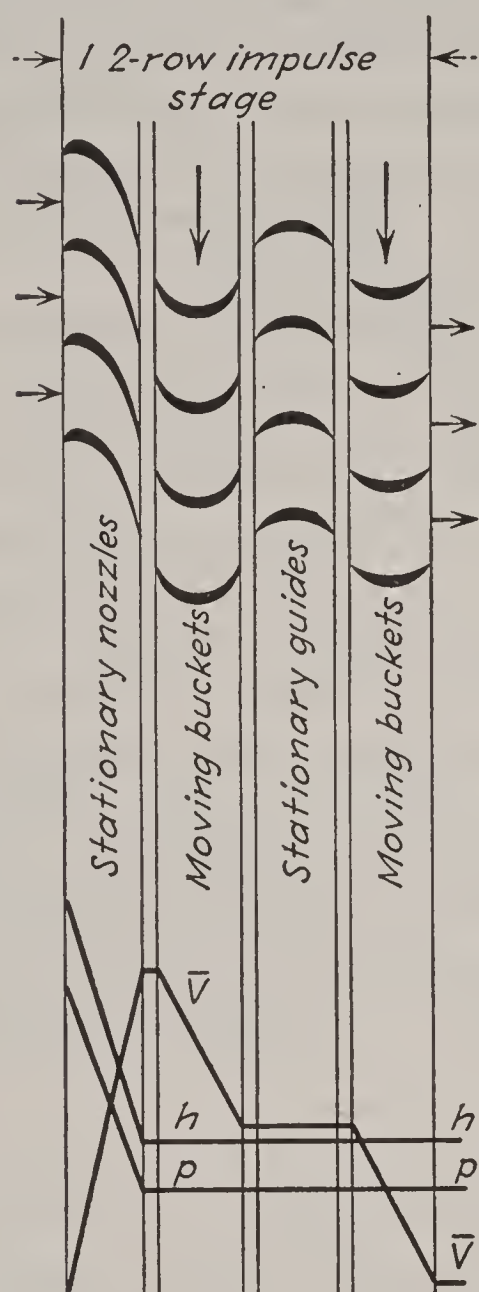


FIG. 11:12. Enthalpy, pressure, and velocity variation through a two-row impulse stage.

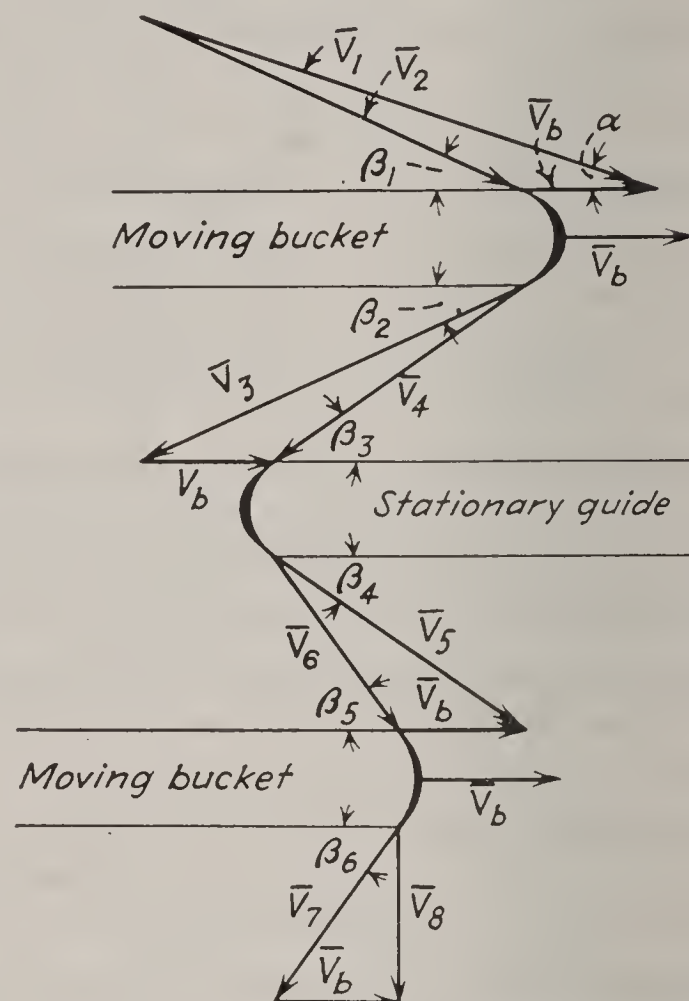


FIG. 11:13. Velocity diagram—two-row impulse stage (maximum work).

conceivable and would be equivalent, respectively, to 9 and 16 single-row stages, but more than two are seldom used because of the mounting frictional losses. Two-row stages are sometimes used for the first drop in pressure in a steam turbine, to be succeeded by single-row stages at the lower pressures.

*Example 11:10.* Assume a reversible single-row impulse stage with an isentropic enthalpy drop of 40 Btu/lb in the nozzles. The nozzle angle is  $20^\circ$ . Calculate, for maximum work on the buckets, (a) the bucket speed, (b) the entry and exit angles of the buckets, (c) the final (residual) velocity of the fluid as it leaves the stage, (d) the force applied on the buckets per pound of fluid flow per second, and (e) the work per pound of flow. Neglect approach velocity to nozzles.



*Solution:*

(a) Referring to Fig. 11:11,  $\bar{V}_1 = (223.8)(40)^{\frac{1}{2}} = 1415$  fps.  
For maximum work,

$$\bar{V}_b = \frac{1}{2} \bar{V}_1 \cos \alpha = \frac{1415 \cos 20^\circ}{2} = \frac{(1415)(0.94)}{2} = 665 \text{ fps}$$

$$(b) \bar{V}_{2x} = \bar{V}_1 \cos \alpha - \bar{V}_b = \bar{V}_1 \cos \alpha - \frac{1}{2} \bar{V}_1 \cos \alpha = \frac{1}{2} \bar{V}_1 \cos \alpha = 665 \text{ fps}$$

$$\beta_1 = \beta_2 = \tan^{-1} \frac{\bar{V}_1 \sin \alpha}{\bar{V}_{2x}} = \frac{1415 \sin 20^\circ}{665} = \frac{(1415)(0.342)}{665} = 0.728$$

or

$$\beta_1 = \beta_2 = 36^\circ$$

$$(c) \bar{V}_4 = \bar{V}_1 \sin \alpha = (1415)(0.342) = 485 \text{ fps}$$

$$(d) F = \frac{\bar{V}_{2x} - \bar{V}_{3x}}{g} = \frac{665 - (-665)}{32.2} = 41.3 \text{ lb per pound of flow per second}$$

$$(e) W = F \bar{V}_b = (41.3)(665) = 27,400 \text{ ft-lb, or } 35.3 \text{ Btu per pound of flow,}$$

Checking this result against the kinetic energy removed from the steam:

$$\frac{\bar{V}_1^2 - \bar{V}_4^2}{2g} = \frac{1415^2 - 485^2}{64.4} = 27,400 \text{ ft-lb}$$

**11:11. Reaction Staging.** Figure 11:14 diagrams a series of four pure reaction stages. Each stage consists of a row of stationary nozzles and a row of moving nozzle buckets. The entry blade angle to both is  $90^\circ$  in the pure reaction stage. (The real reaction stage usually employs a smaller entry angle in order to reduce the required number of stages.) Figure 11:15 shows a velocity diagram for one of these stages. It is observed that the purpose of the stationary nozzles is to give the fluid sufficient velocity so that its velocity relative to the bucket will be in a direction normal to the plane of bucket rotation; this permits the entry angle of  $90^\circ$  mentioned above. The velocity  $\bar{V}_2$  is the approach velocity to the moving nozzle, and the jet velocity is increased to  $\bar{V}_3$  and changed to a rearward direction by the action of that nozzle. In fact the moving nozzle duplicates the expansion of the stationary nozzle, each developing the same exit velocity at the expense of equal enthalpy drops. But the velocity  $\bar{V}_3$  is relative to the moving nozzle bucket and must be vectorially combined with  $\bar{V}_b$  to give  $\bar{V}_4$ , the absolute velocity at exit from the stage (the approach velocity to the succeeding stage). The variation of pressure, enthalpy, and absolute velocity through the series of reaction stages is also included in Fig. 11:14. The pressure and enthalpy drops are continuous through both stationary and moving blades; the curve of absolute velocity resembles that for impulse staging.

Based on the proportions of Fig. 11:15 and following the method used in Art. 11:10, we may write for the reversible pure reaction stage

$$\begin{aligned}\bar{V}_{2x} &= \bar{V}_{1x} - \bar{V}_b = \bar{V}_1 \cos \alpha - \bar{V}_b \\ \bar{V}_{3x} &= -\bar{V}_{1x} = -\bar{V}_1 \cos \alpha \\ W \text{ per lb} &= \frac{(\bar{V}_{2x} - \bar{V}_{3x}) \bar{V}_b}{g} = \frac{(2\bar{V}_1 \cos \alpha - \bar{V}_b) \bar{V}_b}{g}\end{aligned}$$

$$\frac{dW}{d\bar{V}_b} = \frac{2\bar{V}_1 \cos \alpha - 2\bar{V}_b}{g} = 0 \quad \text{or} \quad \bar{V}_b = \bar{V}_1 \cos \alpha \quad (\text{maximum work})$$

$$W_{\max} \text{ per lb} = \frac{2\bar{V}_1^2 \cos^2 \alpha - \bar{V}_1^2 \cos^2 \alpha}{g} = \frac{\bar{V}_1^2 \cos^2 \alpha}{g} = 2 \frac{\bar{V}_1^2}{2g} \cos^2 \alpha$$

As the nozzle angle approaches zero, the approach velocities to both stationary and moving nozzles approach zero and the maximum work of the stage approaches  $2(\bar{V}_1^2/2g)$ . But this is equivalent to the sum of the

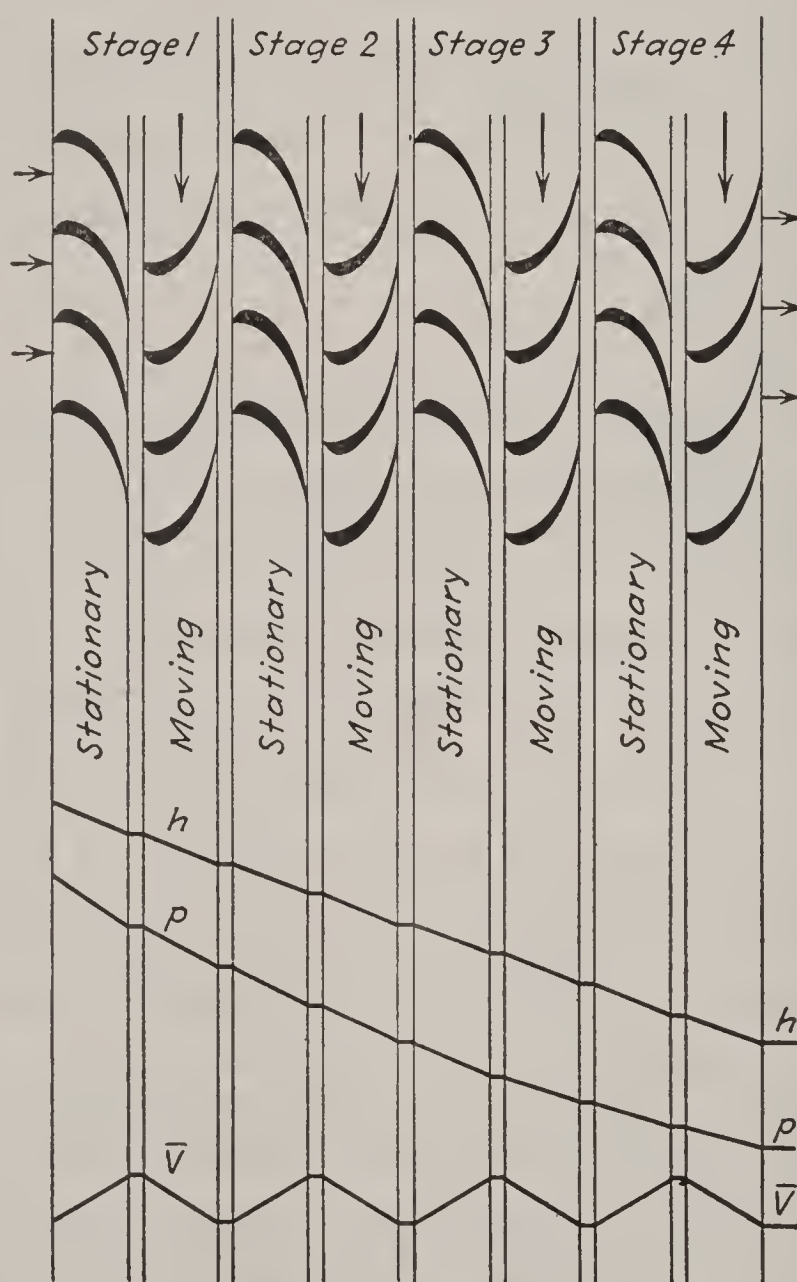


FIG. 11:14. Enthalpy, pressure, and velocity variation through a reaction turbine.

kinetic energies generated in the two nozzles of the stage and therefore to the total stage drop of enthalpy. The reversible character of the process is not altered by giving the angle  $\alpha$  a finite value; this would merely have the effect of providing an approach velocity to each row of nozzles, moving and stationary.



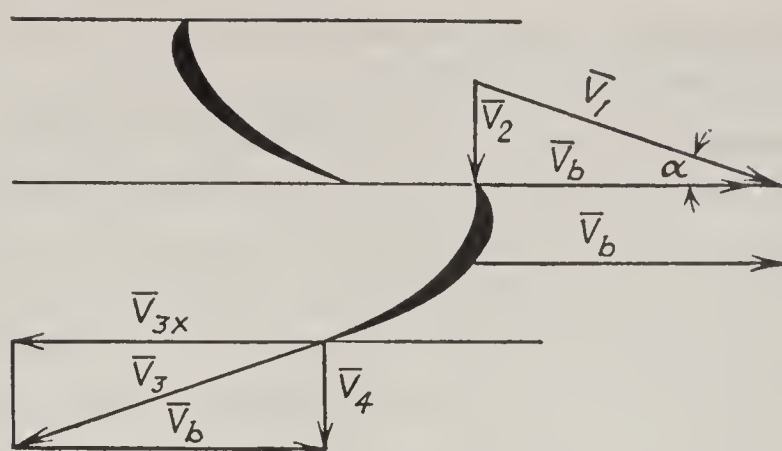


FIG. 11:15. Velocity diagram—reaction stage (maximum work).

*Example 11:11.* The total isentropic enthalpy drop across a reversible pure reaction stage is 40 Btu. The nozzle exit angles of both stationary and moving nozzles are  $20^\circ$ . Neglecting the approach velocity to the stationary nozzles, calculate, for maximum work in the stage, (a) the velocity at exit from the stationary nozzles, (b) the bucket speed, (c) the residual velocity of the fluid as it leaves the stage, (d) the force applied on the buckets per pound of fluid flow per second, and (e) the work per pound of flow.

*Solution:*

(a) Referring to Fig. 11:15, the exit velocity from the stationary nozzles is the approach velocity to the moving nozzles. Some of the kinetic energy developed in the stationary nozzles is therefore utilized in the moving nozzles. This has the effect of increasing the effective enthalpy drop to be divided between the moving and stationary nozzles above the specified 40 Btu for the stage. The enthalpy drop in the stationary nozzles may thus be estimated to approximate 21 Btu, and this would correspond to a velocity leaving the nozzle of  $(223.8)(21)^{\frac{1}{2}} = 1025$  fps. The approach velocity to the moving nozzle would then be  $1025 \sin 20^\circ = 350$  fps, equivalent to an enthalpy drop of  $350^2/2Jg = 2.46$  Btu. The effective enthalpy drop per row of nozzles is therefore  $(40 + 2.46)/2 = 21.23$  Btu. Thus  $\bar{V}_1 = (223.8)(21.23)^{\frac{1}{2}} = 1030$  fps. This differs negligibly from the velocity as estimated above and is the velocity at exit from the stationary nozzles. When the enthalpy drops in moving and stationary nozzles are equal, this is also the velocity  $\bar{V}_3$  of Fig. 11:15. To check, the approach velocity to the moving nozzles is  $\bar{V}_1 \sin 20^\circ = 352$  fps, and the enthalpy drop in the moving nozzle  $40 - 21.23 = 18.77$  Btu/lb. Then, from Eq. (11:1),

$$\bar{V}_3^2 = 352^2 + (223.8)^2(18.77) = 124,000 + 937,000 = 1,061,000$$

or

$$\bar{V}_3 = 1030 \text{ fps}$$

$$(b) \bar{V}_b = \bar{V}_1 \cos 20^\circ = \bar{V}_3 \cos 20^\circ = (1030)(0.94) = 968 \text{ fps} = \bar{V}_{3x}$$

$$(c) \bar{V}_4 = \bar{V}_3 \sin 20^\circ = (1030)(0.342) = 352 \text{ fps}$$

$$(d) F = \frac{\bar{V}_{2x} - \bar{V}_{3x}}{g} = \frac{0 - 968}{32.2} = 30.1 \text{ lb/(lb)(sec)}$$

$$(e) W = F\bar{V}_b = (30.1)(968) = 29,100 \text{ ft-lb, or } 37.5 \text{ Btu/lb}$$

Note that the final kinetic energy in the fluid as it leaves the stage is  $352^2/2Jg = 2.5$  Btu. When this is subtracted from the isentropic drop of enthalpy across the stage, the answer to part e is checked for this reversible stage. Points of interest which develop from a comparison of this solution with that of Example 11:10 are the

higher bucket speed and yet lower leaving loss (residual velocity) characteristic of reaction staging as compared with impulse.

**11:12. Comparison of Impulse and Reaction Staging.** The concept of the pure impulse and pure reaction stages has been based on the assumption of reversibility in flow; reversibility is not attainable in the flow of a real fluid, and the real-turbine stage can be classified as impulse or reaction only in a general sense. For example, some drop in pressure will always accompany the flow of a real fluid through the impulse bucket. However, a comparison of the idealized form of these two types of staging makes it possible to observe differences in design principles which cannot be disregarded in the design of the real turbine. It has been observed that close clearance between the moving bucket and the turbine casing need not be provided in the impulse stage because the drop in pressure across the bucket is small. This is not the case for the reaction stage since a major drop in pressure is maintained through the use of nozzles as buckets; leakage losses are of major importance in the design of the reaction stage. This explains why, in many turbines, impulse stages are used in the earlier, high-pressure stages of expansion, to be followed by reaction staging near the exhaust end of the turbine. The drop in pressure necessary to obtain a given isentropic drop of enthalpy is less in the low-pressure range; a reference to the Mollier diagram in the steam tables will confirm this fact for steam, but it is a common characteristic of all fluids.

The drop in pressure across the buckets of the reaction stage makes it necessary that all buckets take part in the expansion simultaneously instead of only a section of the perimeter at one time, as for the impulse stage; otherwise the leakage of steam through idle-blade spaces could not be prevented. One of the results is that, in the effort to accommodate the greatly increased volume of fluid passing through the later stages of the reaction steam turbine, more dependence must be placed on increasing blade height and increasing rotor diameters. The governing of turbines, to operate at constant speed when the load is variable, is also affected. In the impulse turbine, loads lighter than that for which the turbine was designed may be carried by cutting off the steam flow through a part of the nozzles in each row. This is called *cutoff governing*. This is not feasible as a means of governing the reaction turbine; instead, the *throttle governor* must be used, reducing the pressure of the steam as it is admitted to the reaction stage. This change from the pressure for which the nozzles were designed has the effect of lessening turbine efficiency. Although both impulse and reaction turbines are quite sensitive to changes in speed and load from those for which they were designed, the impulse turbine is somewhat the more flexible, on the basis of its ability to adapt itself to changing loads.

An advantage in using reaction stages for the later stages of expansion



in the steam turbine derives from the increasing percentages of moisture in the steam as expansion proceeds to the lower pressures. This means that particles of dense water are carried in the steam jet as it issues from the nozzle and accounts for a tendency to erode the leading edge of the moving bucket. This effect is greatly reduced in the reaction stage, since the velocity of the entering jet is only that component which is normal to the plane of bucket rotation. Moreover, for the same total stage drop of enthalpy, the thermal energy of the steam is changed into kinetic energy in two steps in the reaction stage, and the maximum velocity reached is therefore only about 70 per cent as large as for the equivalent impulse stage. The desire to reduce erosion is the reason why steam is ordinarily supplied the turbine at high superheat; this reduces the percentage of moisture in the low-pressure stages.

An examination of Figs. 11:10 and 11:11 indicates that the reversible impulse stage would produce no lengthwise (axial) thrust on the turbine shaft; the pressure is balanced on the two sides of the moving buckets, as are the axial components of fluid velocity at entrance and exit. Even in the case of the real impulse-staged turbine, the provision for counteracting thrust need only be minor. Reference to Figs. 11:14 and 11:15 will show that this is not the case for the reaction-staged turbine; the balancing of thrust is an important feature of the design of the reaction turbine.

To utilize the same enthalpy drop at the same blade speed requires, in theory, the provision of twice as many stages of reaction blading as would be necessary if the blading were impulse. The expansion in a single row of stationary nozzles in the impulse turbine produces, in the limit, a velocity of  $2\bar{V}_b$ , which is removed in the following row of buckets. The stationary nozzles of the reaction stage need develop a velocity of only  $\bar{V}_b$ , at the expense of an enthalpy drop only one-fourth as great as for the row of impulse nozzles. Although the buckets of the reaction stage also drop the enthalpy by the same amount, the total stage drop of enthalpy for the reaction stage is thus only half as large as that in the single expansion of an impulse stage having the same bucket velocity. The larger number of stages required is one of the principal factors in making reaction staging more expensive than impulse.

**11:13. Stage Efficiency.** The efficiency of the reversible stage, like that of the reversible nozzle [see Eq. (11:14)] is 1. The efficiency of the real turbine stage is less than 1 only because of irreversibilities that have accompanied the flow of the fluid through the stage. The nature of these irreversibilities and their effect on flow through the nozzle have already been discussed. Let us examine the irreversibilities that are incurred in flow after the stationary nozzle has been passed.

There will always be some drop in pressure across the bucket of a real stage, even if they are shaped like the (impulse-type) blades of Fig. 11:7b.

Thus the pressure at exit from the impulse stage will be at least slightly lower than the pressure at exit from the stationary nozzles. In Fig. 11:16a the coordinates are those of the Mollier chart. The condition of the fluid at entrance to the stationary nozzles is denoted by the position of point 1 and that at exit from the real nozzle as point 2'. The condition at exit from a reversible nozzle is located as point 2, lying on the same line of constant pressure as 2'. The small drop in pressure in the buckets of the impulse stage is the difference between  $p_2$  and  $p_3$ ; in the reversible stage, the work on the buckets per pound of fluid is  $h_1 - h_3$  when this further drop in pressure is considered. Because of irreversibility in flow

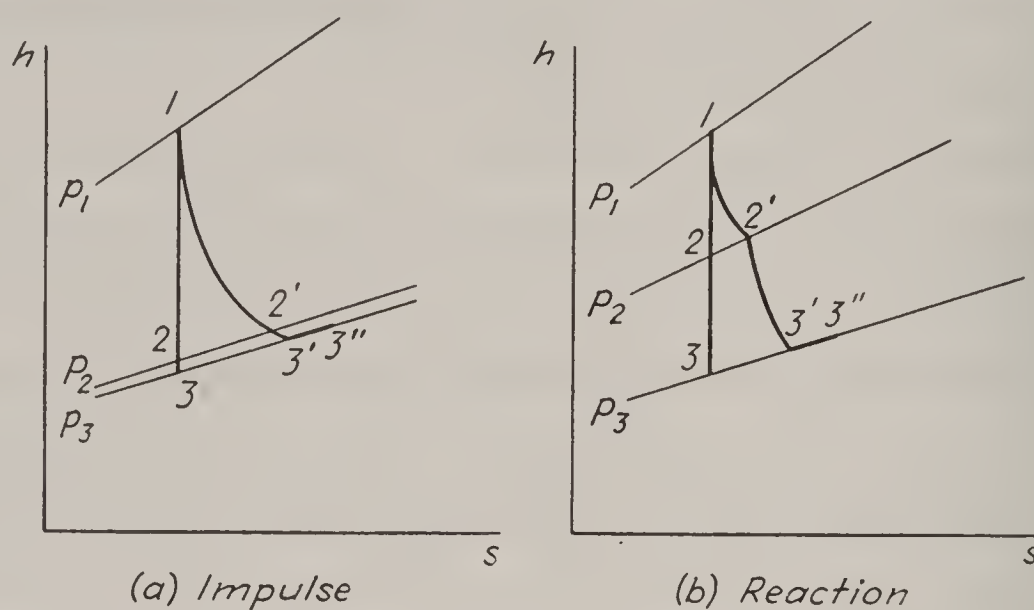


FIG. 11:16. Nozzle-bucket and stage efficiencies.

through the buckets, little of this additional isentropic enthalpy drop is realized in the form of work on the bucket, and the condition at exit from the bucket is represented by the position of point 3'. When Eq. (3:5) is applied to the adiabatic process, using stations at entrance to the stationary nozzle and at exit from the moving bucket and neglecting differences in kinetic energy at these two points, the work performed on the buckets per pound of fluid flow may be shown to be  $h_1 - h_{3'}$ ; the corresponding work for the reversible stage is  $h_1 - h_3$ . The ratio of these enthalpy drops is the *nozzle-bucket efficiency*, or

$$\eta_{nb} = \frac{h_1 - h_{3'}}{h_1 - h_3} \quad (11:25)$$

where the notation is that of Fig. 11:16.

An additional irreversibility occurs outside of either nozzle or bucket and causes the so-called *rotation losses*. The rotating disk on which the buckets are anchored is surrounded by the fluid, and some power is consumed in keeping it moving against the resulting frictional drag. This loss tends to be higher for the impulse stage because some of the buckets are not receiving steam from nozzles and act merely as paddles in stirring



up the fluid. Thus paddle-wheel work is performed on the exiting fluid, and its temperature (or quality) is raised at constant pressure, as indicated by the line 3'-3'' of Fig. 11:16. The increase of enthalpy as the result of rotation losses is  $h_{3''} - h_{3'}$ , and this is at the expense of the work performed on the buckets. Thus the final condition of the fluid as it leaves the stage is represented by the position of point 3'' and the net stage work by the difference  $h_1 - h_{3''}$ . The *stage efficiency* is the ratio of this enthalpy drop to the isentropic drop  $h_1 - h_3$ , or

$$\eta_s = \frac{h_1 - h_{3''}}{h_1 - h_3} = \frac{h_1 - h_{3'}}{h_1 - h_3} - \frac{h_{3''} - h_{3'}}{h_1 - h_3} = \eta_{nb} - \frac{L}{h_1 - h_3} \quad (11:26)$$

where  $L$  is the rotation loss in Btu per pound of fluid passing the stage, and the notation is that of Fig. 11:16.

The terms nozzle-bucket efficiency and stage efficiency have exactly the same meaning when applied to a reaction stage, as in Fig. 11:16b. The only differences between the two diagrams are the smaller drops in pressure in the stationary nozzles and the larger drop in the buckets and the smaller rotation loss indicated for the reaction stage.

**11:14. Turbine efficiency** is the ratio of the work delivered by the turbine per pound of fluid flowing through it to the work delivered by a reversible adiabatic turbine operating between the same inlet state and the same final pressure as the real turbine. The efficiency of a turbine consisting of only a single stage would be identical with the efficiency of that stage.

In Fig. 11:17 is shown a *condition curve* for the series of stages that are included in a turbine. For simplicity, only four stages are shown; the number is often much larger. In fact, if steam is the fluid and there is a total isentropic enthalpy drop of 400 Btu/lb through the turbine, it has been shown in Art. 11:9 that at least eight impulse stages must be employed if the use of expanding nozzles is to be avoided. In Fig. 11:17, the lines labeled  $p_1, p_2, p_3$ , etc., are lines of constant pressure on this Mollier chart and represent the pressures at entrance to the turbine and at exit from each of its stages, respectively. Their slopes increase with increasing temperature, according to Eq. (8:6), and they therefore diverge as shown in the figure. The state of the fluid at entrance to the first stage of the turbine is designated as point 1 and, at entrance to succeeding stages, as 2'', 3'', and 4''. If the expansion through the turbine had been isentropic, the final state would have been as designated by the position of point 5, and the work of the ideal turbine is therefore  $h_1 - h_5$ . The work actually delivered by the turbine is the same as the sum of the work delivered by the individual stages, or  $(h_1 - h_{2''}) + (h_{2''} - h_{3''}) + (h_{3''} - h_{4''}) + (h_{4''} - h_{5''}) = h_1 - h_{5''}$ . Based on the definition of turbine efficiency,

$$\eta_t = \frac{h_1 - h_{5''}}{h_1 - h_5} \quad (11:27)$$

where  $\eta_t$  is the turbine efficiency, a decimal fraction, and the notation is that of Fig. 11:17.

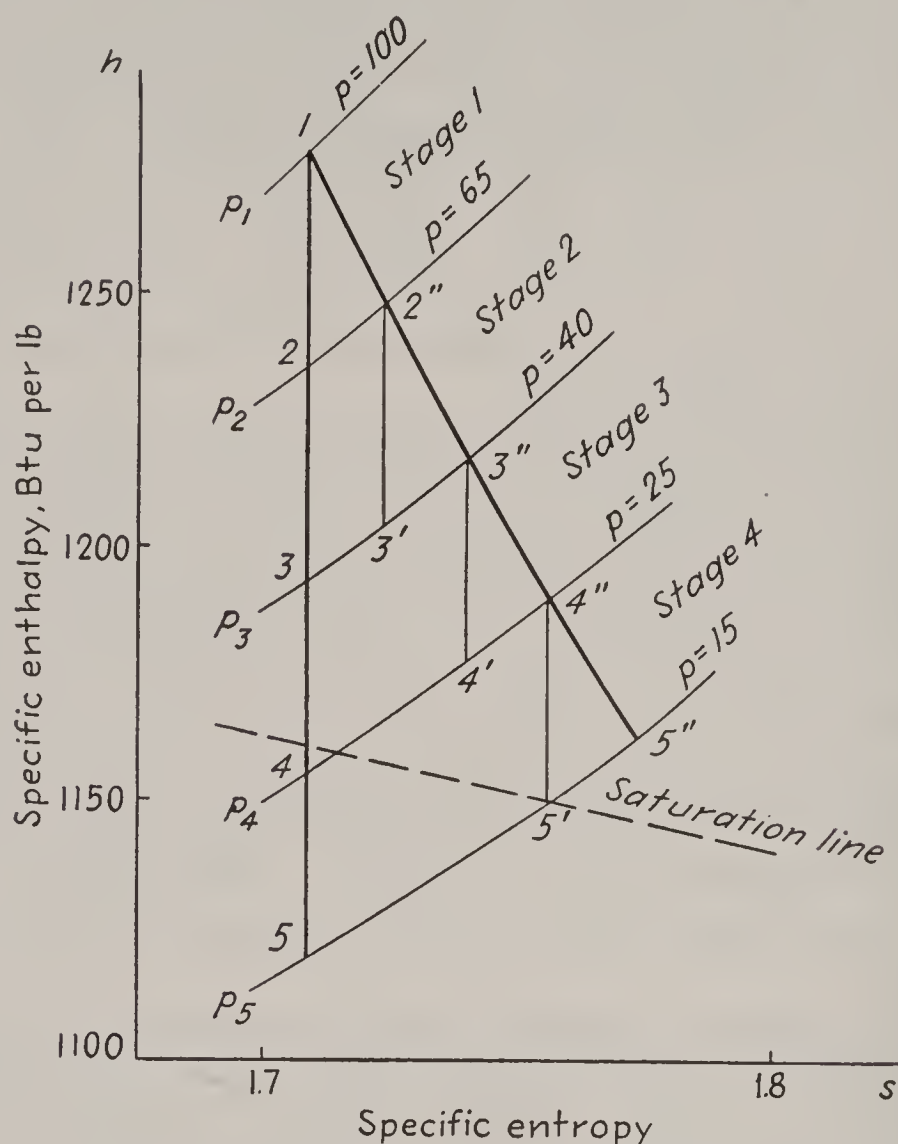


FIG. 11:17. Turbine condition curve (data from Example 11:14).

Point 2'' in Fig. 11:17 corresponds to the state of the fluid at entrance to the second stage (or to point 3'' of Fig. 11:16). From Eq. (11:26), the efficiency of the first stage, based on the notation of Fig. 11:17, is

$$\eta_{s1} = \frac{h_1 - h_{2''}}{h_1 - h_2}$$

Similarly, the efficiencies of the succeeding stages are, respectively,

$$\eta_{s2} = \frac{h_{2''} - h_{3''}}{h_{2''} - h_{3'}} \quad \eta_{s3} = \frac{h_{3''} - h_{4''}}{h_{3''} - h_{4'}} \quad \eta_{s4} = \frac{h_{4''} - h_{5''}}{h_{4''} - h_{5'}}$$

and the average efficiency of all the stages may be written as

$$\eta_{s_{avg}} = \frac{h_1 - h_{5''}}{(h_1 - h_2) + (h_{2''} - h_{3'}) + (h_{3''} - h_{4'}) + (h_{4''} - h_{5'})} \quad (11:28)$$

Because of the divergence of the lines of constant pressure on the chart,



the denominator of Eq. (11:28) is larger than the denominator of Eq. (11:27). But the numerators are identical, and it is therefore evident that *the efficiency of the multistaged turbine is greater than the average efficiency of its stages.*

**Example 11:14.** Steam enters a turbine that has four single-row impulse stages at 100 psia, 500°F. The pressures at exit from the stages are 65, 40, 25, and 15 psia. The stage efficiencies are each 70 per cent. Neglecting the approach velocity to each stage, calculate (a) the temperature or quality at entrance to each stage, (b) the work per pound of steam expanded, and (c) the efficiency of the turbine.

*Solution:*

(a) With reference to the notation of Fig. 11:15 and employing the Mollier diagram for steam,  $h_1 = 1279$ ;  $h_2 = 1237$ ;  $h_3 = 1194$ ;  $h_4 = 1156$ ;  $h_5 = 1120$ ;  $h_{2''} = 1279 - 0.70(1279 - 1237) = 1250$  Btu. This corresponds to a temperature of about 435°F at entrance to the second stage and locates point 2''.

Returning to the chart and projecting vertically from point 2'' to a pressure of 40 psia,  $h_{3'}$  is read as 1206 Btu. Then  $h_{3''} = 1250 - 0.70(1250 - 1206) = 1219$  Btu. At 40 psia, this enthalpy corresponds to a temperature of about 363°F. This is the condition of the steam at entrance to the third stage and locates point 3''.

Proceeding in a similar manner,  $h_{4'}$  is read from the chart as 1179 Btu and  $h_{4''} = 1219 - 0.70(1219 - 1179) = 1191$  Btu. At 25 psia, this corresponds to a temperature of about 301°F and locates point 4''.

Also,  $h_{5'}$  is read from the chart as 1151 Btu and  $h_{5''} = 1191 - 0.70(1191 - 1151) = 1163$  Btu. This enthalpy, at 15 psia, corresponds to a temperature of about 238°F and locates point 5''.

(b)  $\frac{W}{J} = h_1 - h_{5''} = 1279 - 1163 = 116$  Btu per pound of steam

(c) Turbine efficiency  $= \frac{h_1 - h_{5''}}{h_1 - h_5} = \frac{116}{1279 - 1120} = 0.73$

**11:15. The Axial-flow compressor** is essentially a reaction turbine operated in reverse; it is sometimes an important part of the apparatus necessary to demonstrate the cycle of the gas turbine, to be discussed in Chap. 12. It is staged to make it possible to compress gases such as air to high pressures without incurring serious irreversibility due to high velocity. The blading is similar to the reaction blading shown in Fig. 11:14 (though the angle relations are different in order that the blades may be better adapted for their new function), but the fluid enters at the right at low pressure and is discharged, at what would be the inlet to the turbine, at high pressure; the direction of bucket movement is opposite to that shown in the figure, and power is supplied from some external agency to drive the rotor. The moving buckets receive the fluid and increase its velocity, at the same time acting as diffusers in increasing the pressure; the stationary blades continue the diffuser action. The graphs of pressure, enthalpy, and velocity shown in the figure also apply to the axial-flow compressor but are traced from right to left.

The condition line for the fluid passing through the axial-flow com-

pressor is shown in Fig. 11:18. The compression is, ideally, isentropic, and the work ideally required for the compression of unit weight is  $h_5 - h_1$ . Because of irreversibility, the final condition of the fluid is at  $5''$ , and the

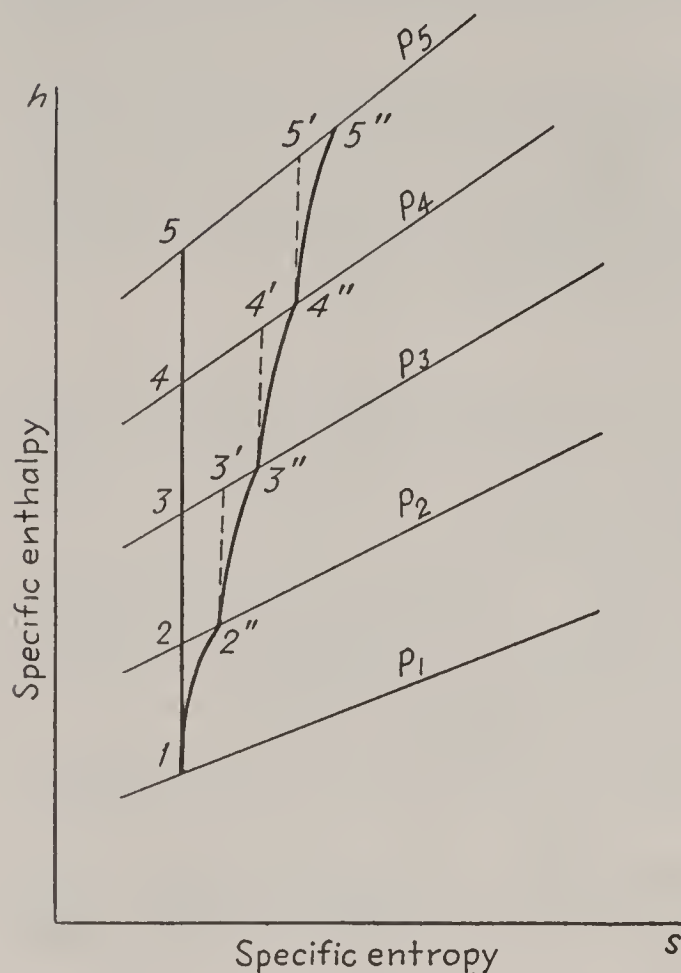


FIG. 11:18. Condition curve—axial-flow compressor.

work required for compression is  $h_{5''} - h_1$ , greater than  $h_5 - h_1$ . The ratio  $(h_5 - h_1)/(h_{5''} - h_1)$  is called the *adiabatic efficiency*.

The thermodynamic principle is the same for the axial-flow compressor as for the adiabatic reciprocating compressor, discussed in Chap. 9. This type of compressor is used when a continuous-flow type of compression is desirable and when its advantages of somewhat higher efficiency and lower frontal area (an advantage that is important when the compressor forms a part of an airplane power plant, because of lowered air resistance) give it preference over the centrifugal compressor. The pressure ratio per stage approximates 1.2:1, and a relatively large number of stages

are needed to obtain a given over-all pressure ratio; this means that it has the disadvantages of greater length and weight as compared with the centrifugal compressor.

### Problems

1. A fluid flows through a horizontal channel. As it moves from an upstream section to a downstream section, its specific enthalpy decreases by 150 Btu/lb. If the velocity at the upstream section is 600 fps and the flow is adiabatic (though not frictionless), what is the velocity at the downstream section?

2. A circular opening permits the passage of 2400 lb of steam per hour. If the velocity is 2000 fps and the steam has a density of 0.25 lb/ft<sup>3</sup> in the opening, what is its diameter in inches?

3. As a fluid flows adiabatically through a horizontal channel, the velocity at an upstream section is 1000 fps. At a downstream section of the channel, the velocity is 2500 fps. What is the change of specific enthalpy between the two sections?

4. An incompressible fluid is held in a tank. A horizontal nozzle is located in the wall of the tank at a level where the pressure inside the tank is steadily maintained at 150 psia, and the liquid issues to the atmosphere through this nozzle. Assuming the flow to be isentropic, calculate the velocity of the issuing jet (a) if the density of the liquid is 62 lb/ft<sup>3</sup> and (b) if its density is 30 lb/ft<sup>3</sup>.

5. Considering them to be perfect gases, calculate the critical pressure ratios for (a) carbon dioxide; (b) water vapor; (c) methane (CH<sub>4</sub>) [ $c_v = 0.45$  Btu/(lb)(°F)].



6. Air approaches a given nozzle with negligible velocity and at a pressure of 100 psia. The pressure in the space to which the nozzle discharges is atmospheric. Will the mass rate of flow through the nozzle increase, decrease, or remain the same if the following individual changes are made in supply and exhaust pressures? (a) The discharge pressure is reduced to 5 psia. (b) The discharge pressure is raised to 30 psia. (c) The discharge pressure becomes 70 psia. (d) The supply pressure increases to 120 psia. (e) The supply pressure becomes 60 psia.

7. Calculate the velocity of sound in the following perfect gases at a temperature of 70°F: (a) air; (b) water vapor; (c) carbon dioxide; (d) helium; (e) hydrogen; (f) methane (see Prob. 5).

8. Air enters a reversible adiabatic nozzle at 100 psia, 200°F, and at low velocity. The discharge pressure is atmospheric. What is the temperature of the air at the throat of the nozzle? What is its velocity? Calculate the velocity of sound in air at the throat temperature, and compare.

9. In a wind tunnel the model to be tested is held stationary in a moving stream of air, and the resulting forces and moments are measured. When the air is to be given high velocity, the nozzle principle may be used by allowing the air to pass through a constricted channel as the result of a pressure differential which is maintained between its two ends. If the tests are to be made in the supersonic range (above the velocity of sound), discuss the necessary pressure differential and the location of the test section in the passage.

10. Design a nozzle of round cross section to expand 3000 lb of air per hour from an initial pressure (at negligible velocity) of 140 psia and a temperature of 350°F to a final pressure of 15 psia. Assume frictionless adiabatic flow.

11. Air enters a converging-diverging passage at 20 psia, 100°F, and with a velocity of 2000 fps. The area at the throat of the passage is 1 in.<sup>2</sup>; the area at exit from the passage is large enough so that the velocity at that point may be considered negligible. Assuming the flow to be adiabatic and reversible, calculate (a) the temperature and pressure of the air at the exit and (b) at the throat.

12. Assuming that the flow is adiabatic and reversible, find the required throat and exit areas of a nozzle to expand 3000 lb of steam per hour from 140 psia, quality of 0.98, to a final pressure of 15 psia. The entrance velocity is negligible.

13. In Prob. 12, change entry conditions to 140 psia and 400°F, and design the nozzle.

14. Redesign the exit areas of the nozzles of Probs. 10, 12, and 13 on the basis of an expected nozzle efficiency of 0.88. In each case, discuss the change in the properties of the fluid as it leaves the nozzle. What is the velocity coefficient?

15. Assuming a discharge coefficient of 0.99 will apply, determine the required throat areas in Probs. 10, 12, and 13.

16. In Prob. 13, assume that the steam was supersaturated as it passed the throat of the nozzle, and calculate the coefficient of discharge for frictionless flow. At what maximum temperature could the steam have been supplied to give a coefficient of discharge greater than 1?

17. Work Example 11:10 with the following changes in data: isentropic enthalpy drop = 100 Btu/lb; nozzle angle = 18°. Draw, to scale, a velocity diagram of the stage.

18. Steam is supplied a reversible single-row impulse stage at 140 psia, 400°F, and at negligible velocity. The pressure at exhaust from the stage is 15 psia. The nozzle angle is 20°. Calculate, for maximum work on the buckets, (a) the bucket speed, (b) the entry and exit angles of the buckets, (c) the final velocity of the steam as it leaves the stage, (d) the force applied on the buckets per pound of steam flow per second, and (e) the work per pound of flow.

19. The data are the same as for Prob. 18 except that the stage is a two-row reversible impulse stage. The nozzle angle is  $20^\circ$  at entrance to the first row of buckets. Find, for maximum work per pound of steam, (a) the bucket speed; (b) the angle at which the steam is directed on the second row of buckets, relative to their plane of rotation; (c) the entrance and exit angles of both rows of buckets; (d) the force applied on the first row of buckets per pound of steam per second and on the second row; (e) the work per pound of flow delivered to each row of buckets. Draw, to scale, a velocity diagram of the stage.

20. A reversible single-row impulse stage is designed to give maximum work when the bucket speed is 900 fps. The nozzle angle is  $20^\circ$ . (a) What is the enthalpy drop across the nozzles if the approach velocity is negligible? (b) What is the net enthalpy drop for the stage when effect is given to the residual velocity of the steam as it leaves the stage?

21. The same as Prob. 20, except that the stage is a two-row reversible impulse stage. A three-row stage.

22. If the velocity of sound in steam approximates 1700 fps at the state which exists in a reversible pure reaction stage having nozzles of the form shown in Fig. 11:14, what is the approximate maximum total enthalpy drop for which the stage may be designed?

23. Work Example 11:11 with the following changes in data: isentropic enthalpy drop across the stage = 60 Btu/lb; nozzle exit angles =  $25^\circ$ .

24. Steam enters a reversible pure reaction stage at 10 psia, quality of 0.98, and at negligible velocity. The nozzle exit angles are  $25^\circ$ , and the bucket speed is 800 fps. The stage work is a maximum. What is the condition (pressure, quality, and velocity) of the steam at exit from the stage? What work is performed in the stage per pound of steam? If the steam leaving the stage is slowed reversibly to negligible velocity as it approaches the following stage, what is its state as it enters that stage?

25. Steam is admitted to a turbine at 400 psia,  $600^\circ\text{F}$ . Condenser pressure is 1 psia. Assuming zero nozzle angles and a bucket speed of 500 fps for all stages, calculate the minimum number of stages required for a reversible turbine if the stages are all (a) impulse single-row; (b) impulse two-row; (c) impulse three-row; (d) reaction.

26. Steam is supplied a single-row impulse stage at 140 psia,  $400^\circ\text{F}$ , and at negligible velocity. The pressure at exhaust from the stage is 15 psia. The nozzle-bucket efficiency is 0.60, and the stage efficiency is 0.57. What is the rotation loss in the stage in Btu per pound of steam? What is the state of the steam as it leaves the stage?

27. The enthalpy drop across a stage is 100 Btu per pound of steam. The stage efficiency is 0.55, and the rotation loss is 4 Btu per pound of steam. What is the nozzle-bucket efficiency?

28. Steam enters a turbine that has three single-row impulse stages at 140 psia,  $400^\circ\text{F}$ , and at negligible velocity. The pressure at the turbine exhaust is 15 psia. The turbine efficiency is 0.65. If equal work is performed in each stage and the stage efficiencies are equal, find the pressures at entrance to the second and the third stages. What are the stage efficiencies?

29. Steam enters a turbine that has four single-row impulse stages at 140 psia,  $400^\circ\text{F}$ , and at negligible velocity. The pressure at the turbine exhaust is 15 psia. The first stage has an efficiency of 0.58, the second 0.60, the third 0.62, and the fourth 0.64. Equal work is performed in all stages. By trial and error, locate the pressures at entrance to the second, third, and fourth stages, and calculate the turbine efficiency. Plot the condition curve on the Mollier diagram. (Note: A method of attack on this problem consists in assuming a *reasonable and consistent* turbine effi-



ciency, locating the state at exit from the turbine on the basis of this assumption, and checking the assumption against the given data.)

30. Air enters an axial-flow compressor at 14.7 psia, 70°F, and is compressed to 140 psia. The adiabatic efficiency of the compression is 0.80. At what temperature does the air leave the compressor? How much work is done on each pound of air? Approximately how many stages would be needed?

### Symbols

$A$	area
$c_p$	specific heat at constant pressure
$C_{v_n}$	coefficient of velocity of a nozzle
$C_d$	coefficient of discharge
$F$	force
$g$	acceleration of gravity
$h$	enthalpy of unit mass
$J$	proportionality factor
$k$	ratio of the specific heats
$L$	rotation loss
$M$	mass rate of flow
$n$	a constant exponent
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow per unit mass rate of flow
$R$	gas constant
$s$	entropy of unit mass
$t$	scalar temperature
$T$	absolute temperature
$u$	internal energy of unit mass
$v$	specific volume
$\bar{V}$	velocity
$W$	rate of work delivery per unit mass rate of flow
$z$	elevation

### Greek Letters

$\alpha$	nozzle angle to plane of rotation of the bucket
$\beta$	bucket angle to plane of rotation
$\eta_n$	nozzle efficiency
$\eta_{nb}$	nozzle-bucket efficiency
$\eta_s$	stage efficiency
$\eta_t$	turbine efficiency

### Subscripts

av	average
$b$	bucket
$i$	ideal
max	maximum
$n$	nozzle
$nb$	nozzle bucket
$p$	constant pressure
$s$	constant entropy; also, stage
$t$	turbine
$v$	constant volume

## CHAPTER 12

### POWER—GAS SYSTEMS

**12:1. Introduction.** For the production of power (the *continuous* manufacture of work) the use of some sort of cycle is indicated. In developing the basic concepts of thermodynamics, the heat-engine cycle has been used; it will be remembered that only heat and work may pass the boundaries of the heat engine. The Carnot and Stirling engines, introduced and described in Chap. 4, are examples of the heat engine, and both are typically associated with the gas system. The Carnot engine, for reasons discussed earlier, is a purely theoretical device and is not built in the form of a practical engine. The Stirling, on the other hand, in spite of the complexities and irreversibilities introduced by regeneration, was one of the first real engines to be based on the use of a gas system; its cycle was proposed by Robert Stirling in 1827.

Heat enters both the Carnot and Stirling engines through the head of the cylinder; this cylinder therefore adds the functions of a heat exchanger to its duties in connection with the development of power. In Chap. 6 it has been brought out that, for maximum efficiency, heat should be received at as high an average temperature as is feasible and should be rejected at the lowest practical average temperature. The engineer normally provides the heat supply by a process which involves the combustion of fuels; by means of this process, the temperature of the source can be maintained at 3000 to 4000°F. But this heat can be induced to enter the cylinder only by maintaining a differential of temperature between the outside and the inside of the cylinder. The highest temperature that can be attained by the working substance is limited by the *metallurgical limit* of the materials used in the construction of the real cylinder. This is the highest temperature at which the walls can be trusted to retain a strength consistent with their other duties, such as the confinement of a fluid under pressure; it is about 1000°F for the metals ordinarily used by the engineer. Thus the *effective* source temperature (the maximum temperature attained by the enclosed system) must be below this metallurgical limit, and the attainment of high efficiencies is correspondingly handicapped.

To avoid the limitation placed on the effective source temperature by factors such as the metallurgical limit, most gas-system power cycles employ *internal combustion*. Combustion takes place, in other words, within the engine. To prevent the walls from attaining too high a tem-



perature, a cooling fluid (usually water or air) flows around the cylinder. Here the differential of temperature is in the opposite direction, and, with effective cooling, the walls may be prevented from reaching a level of temperature above that at which they may properly carry out their other functions.

**12:2. The Air-standard Cycle.** The process of combustion is, in practice, an irreversible process, and, to make continuous operation of the internal-combustion engine possible, fresh supplies of fuel and air must be introduced, either intermittently or continuously, during the operation of the engine. Thus the internal-combustion engine not only receives heat and work across its boundaries but also accepts matter in the form of fuel and air and rejects it in the form of the products of combustion; it is therefore not a heat engine.<sup>1</sup>

The internal-combustion engine does, however, operate on a cycle. This cycle may be read as the path traced on an indicator diagram taken during the operation of the engine and may conveniently be termed a cycle of the *machine*. The process of combustion will be represented on this diagram by a line, which may be a constant-volume, constant-pressure, constant-temperature, or some other sort of process which has been followed as the result of combustion, according to the conditions under which that combustion took place. Essentially, the same line could have been traced if heat had been supplied a closed system consisting of air alone, if the conditions that existed during the supply of that heat had been similarly controlled. Note that, in that case, no change in weight or in chemical composition need have taken place and the system could be handled as if composed of a pure substance. Similarly, the rejection of heat may substitute for the expulsion of the products of combustion, since it is no longer necessary to replace the charge. These two substitutions are introduced into what is called the *air-standard cycle*.

The concept of the air-standard cycle makes it possible to change the machine cycle of the internal-combustion engine into an equivalent heat-engine cycle. It is our purpose to show the effects of various changes in the conformation of the cycle on the operating characteristics and the efficiency of the internal-combustion engine. This would be very difficult, if we did not make use of this new concept, because of the large num-

<sup>1</sup> The process of combustion is, within certain limits, reversible. At extremely high temperatures, the products of combustion, formed at lower temperature, tend to dissociate into the reactants. If advantage may ultimately be taken of this behavior, much higher efficiencies may be hoped for than characterize the present-day heat engine. This possibility will receive more detailed attention in Chap. 19.

Also, although the internal-combustion engine alone does not operate on a closed cycle, the cycle may be imagined as closed by including the effect of the processes of nature, which acts on the products of combustion to return them eventually to the form of the reactants.

ber of interacting factors, such as changes in composition of the charge and its variable weight throughout the cycle, variable specific heats, and the effects of dissociation, that would necessarily be considered. The efficiency of the air-standard cycle, on the other hand, may be quite easily calculated in advance of the construction of the engine and indicates the maximum conceivable efficiency of an engine operating on that cycle. Although the real engine cannot attain so high an efficiency as that of the air-standard cycle, the ratios of the efficiencies of two air-standard cycles will serve as a valuable guide in the comparison of the two cycles. Also, the ratio of the actual efficiency of the real engine to the efficiency of its equivalent air-standard cycle is of some assistance in estimating the ratio of actual to perfect performance for that engine. This ratio will usually be about one-half to two-thirds; if it is much less than the lower figure, it is possible that improvement in design or operating conditions may result in worth-while gains. Of course, in the more advanced design stage, the factors ignored in the concept of the air-standard cycle must be taken into account.

Other purposes are served as well by an analysis of the air-standard cycle as by the more complicated and laborious examination of the cycle of the real internal-combustion engine. For example, the general effect of changes in the precombustion treatment of the charge, and of changing the amount of fuel burned per cycle, may be shown. Also, a thermodynamic study of the air-standard cycle may suggest changes in the cycle itself that would be advantageous if they can be applied to the real engine and so may lead to an entirely new, and more satisfactory, cycle.

**12:3. The Otto Engine.** The operation of the internal-combustion engine in most common present-day use is based on the cycle proposed in 1862 by Beau de Rochas. An engine to operate on this cycle was first built in 1876 by Otto, a German engineer, and both cycle and engine are now known by his name. A schematic diagram, showing some of the essential features of the Otto engine, is presented in Fig. 12:1. Its idealized cycle of operation, as suggested by Beau de Rochas, is shown in Fig. 12:2. The engine and its cycle here illustrated are of the four-stroke-cycle type in which four strokes of the piston (two revolutions of the engine shaft) are required to complete the cycle; two-stroke-cycle operation is also made possible by certain changes in the position of the valves and their method of operation and in the method of introducing the fuel mixture into the cylinder. Thermodynamically, as will be explained below, the four-stroke cycle becomes a two-stroke cycle when the concept of the air-standard cycle is introduced.

Referring to Fig. 12:1, the downward motion of the piston on the suction stroke, with the intake valve open, draws a charge of air through the intake line. On its way to the cylinder, fuel is drawn into this stream of



air in the carburetor, or mixing valve. This fuel may be either a volatile liquid, such as gasoline, or a fuel gas, such as natural gas; if the former, a carburetor is employed and, if the latter, a simple mixing valve. During the remainder of its passage to the cylinder, the fuel and air become thoroughly mixed.

At the proper point in the cycle that takes place within the cylinder, as described below, a spark is introduced into this mixture by an electrical system consisting of a battery and coil, or magneto, a timer, or distributor, and a spark plug set into the top of the cylinder. Since all of the fuel and

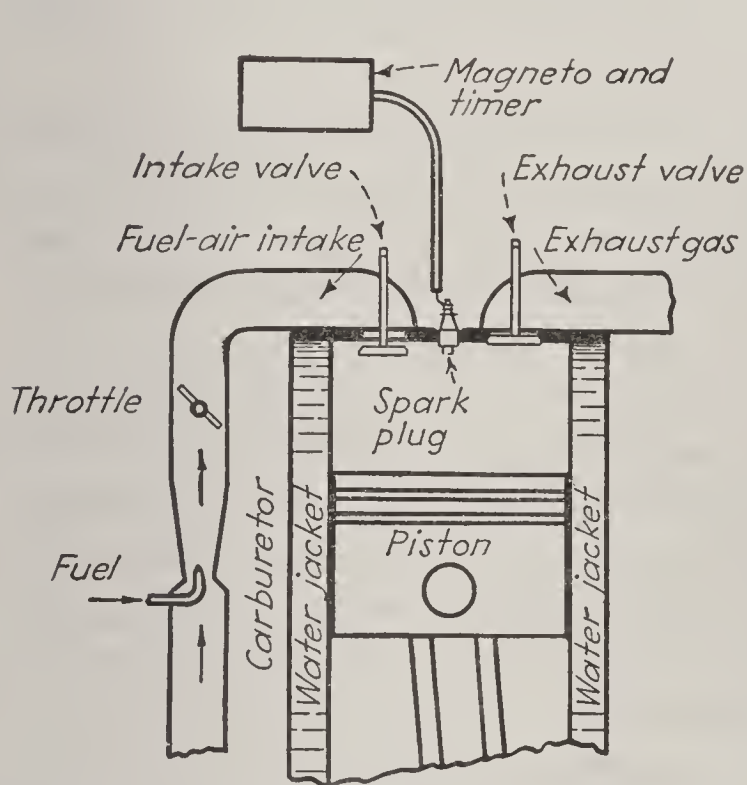


FIG. 12:1. Internal-combustion engine—Otto cycle.

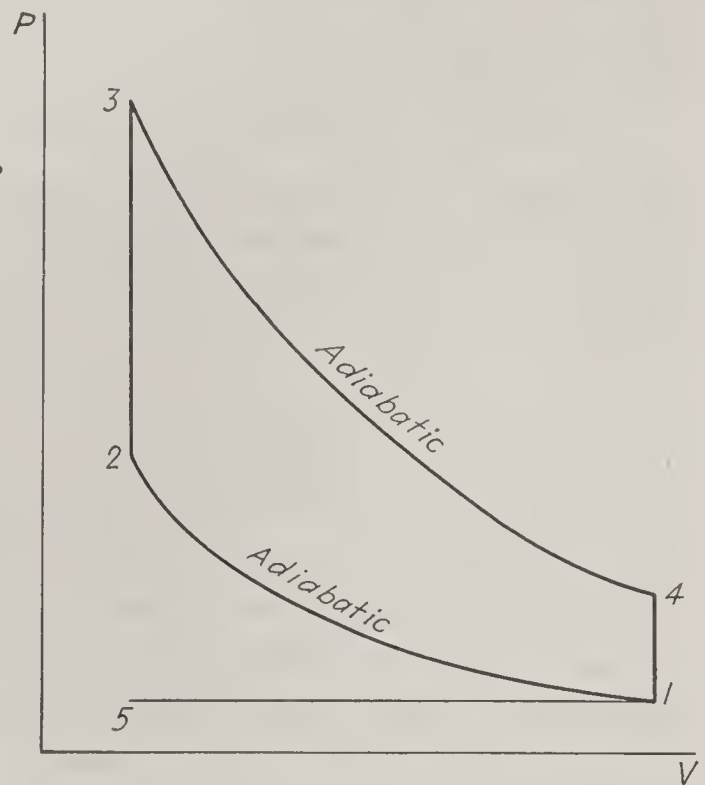


FIG. 12:2. Otto cycle.

all of the air necessary to its combustion are present, an *explosion* takes place. The final step in the cycle is the rejection of the burned gases to the atmosphere through the exhaust valve, preparatory to the entry of a fresh charge into the cylinder. The reciprocating motion of the piston is converted into rotary motion by means of the connecting rod and crank, and some sort of flywheel is necessary to store energy during the single power stroke and return it during the balance of the cycle.

The water jacket shown here may be replaced by thin fins for direct air cooling. Cooling is necessary to protect the materials of which the cylinder and piston are fabricated at the high temperatures that are developed within the cylinder; it is not necessary, or even desirable, in a strictly thermodynamic sense. The difficulty of properly cooling the piston accounts for the prevalence of the single-acting engine in internal-combustion design. The engine is governed by changing the position of the throttle valve at the top of the carburetor; this changes the weight of

fuel mixture taken into the cylinder without materially affecting the proportions of fuel to air.

The detailed operations that take place within the cylinder are outlined below with reference to Fig. 12:2.

1. A *suction stroke*, 5-1, during which a mixture of air and fuel is drawn into the cylinder at constant pressure; during this stroke the intake valve is open, the exhaust valve closed.

2. Near the end of the suction stroke, the intake valve is closed mechanically, the piston reverses its direction of motion and, with both valves closed, carries out the *compression stroke*, 1-2. The mixture is compressed approximately adiabatically during this stroke, and the temperature of the charge rises with its pressure.

3. Near the end of the compression the spark is introduced, exploding the charge while the piston is approximately stationary. The release of the heat of combustion thus takes place at nearly constant volume and raises the temperature and pressure, as indicated by the line 2-3 of Fig. 12:2.

4. As the piston again changes its direction of motion, with both valves still closed, the *expansion stroke*, 3-4, provides for approximately adiabatic expansion of the products of combustion; during this stroke the temperature gradually decreases. Near the end of the expansion stroke, the exhaust valve opens, and a part of the burned gases escapes from the cylinder as the pressure drops along the line 4-1; this is a throttling operation but is not strictly steady-flow in character.

5. The last stroke of the piston necessary to complete the cycle rejects the remainder of the burned gases at constant pressure as indicated by the line 1-5 of Fig. 12:2; this is called the *exhaust stroke*. Near the end of this stroke, the exhaust valve closes, and the intake valve opens, preparatory to retracing the cycle of operations described above.

This cycle may be completed in two strokes of the piston instead of the four outlined above by providing for rejection of the burned gases and injection of a new charge at the end of the expansion and the beginning of the compression strokes. In real engines based on the Otto cycle, certain practical considerations, such as weight, size, cost, simplicity, and fuel economy, may cause preference to be given either the four-stroke or the two-stroke cycle.

In converting the cycle described above to an equivalent air-standard cycle, the charge is air and air alone, and the same charge is used in successive traversals of the cycle. This makes the suction and exhaust strokes, 5-1 and 1-5, unnecessary, and the air-standard cycle becomes a two-stroke cycle. Also, the air-standard engine would, like the Carnot engine, require no valves. The combustion process 2-3 is replaced by the addition of heat in sufficient amount to bring about this rise in pressure at



constant volume, and the pressure drop 4-1 is accomplished by the extraction of heat in appropriate amount. Furthermore, these processes are conceived as reversible processes, thus requiring that the concepts of a variable-temperature source and a variable-temperature refrigerator be introduced. The compression and expansion strokes, 1-2 and 3-4, are idealized as reversible and adiabatic in the Otto air-standard cycle. Noting that all processes of which it is comprised are individually reversible, we observe that the Otto air-standard cycle is a reversible cycle. However, its reversibility does not compare with that of the Carnot and Stirling cycles, which were designed to receive heat from a source *at constant temperature* and to reject heat to a refrigerator at some lower, but *constant*, temperature.

To make the comparison between the air-standard Otto and the Carnot cycles more vivid, let us place them on the same  $TS$  diagram, as shown in Fig. 12:3. On this figure, the Otto air-standard cycle is shown as 1-2-3-4. This is a reversible cycle, and a comparative idea of its efficiency may be obtained by comparing the area enclosed within the cycle with the area 6-2-3-5 under the line 2-3, representing the heat-supply process.<sup>1</sup> But there is available to the engineer, through the process of combustion,

what amounts to a constant-temperature source at between 3000 and 4000°F. This means that the temperature at point 3 may lie in this range. The basic refrigerator is the atmosphere, also characterized by a constant temperature, and it is evident that the lowest temperature of the cycle (at point 1) cannot fall below that of the atmosphere. If we conceive a Carnot engine operating between these constant temperatures of source and refrigerator, its cycle would be traced as 1-2c-3-4c of Fig. 12:3 and its efficiency is  $\frac{\text{area } 1-2c-3-4c}{\text{area } 6-2c-3-5}$ . The advantage of the Carnot in respect to its efficiency is evident; its disadvantage is that its performance cannot be translated into terms of the operation of a real engine, while real Otto engines may be built and operated.

Before leaving Fig. 12:3, let us note that, as the temperature rise during

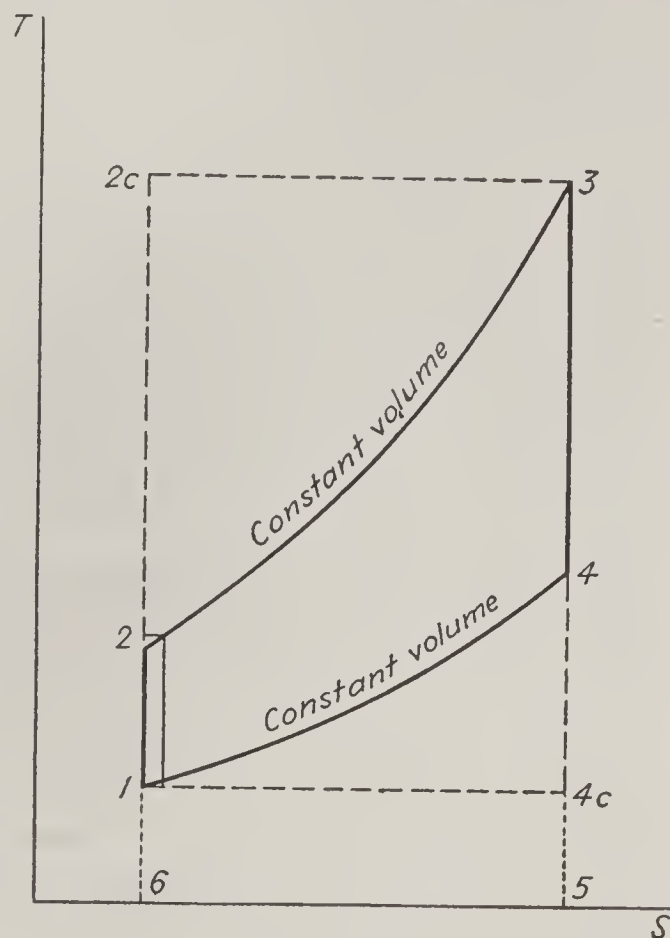


FIG. 12:3. Comparison of Otto air-standard and Carnot cycles.

<sup>1</sup> For the basis of this statement, the reader is referred to Art. 6:5.

combustion decreases, point 3 will move downward along the curve 3-2 toward point 2. Let us assume that this decrease in the heat supply to the air-standard cycle has been carried to the point where point 3 is only infinitesimally to the right of and above point 2. The result is shown in the small cycle which is pictured as lying alongside the isentropic compression line 1-2; it is evident that, as the heat supply decreases, the efficiencies of the Otto air-standard and of the Carnot cycles approach each other. This is, however, of little importance in the application of the cycle as the basis of the operation of a real engine. It will be noted that the small Carnot cycle has an efficiency much less than that of the large Carnot cycle, which, in turn, was based on the available temperatures at which heat could be supplied and rejected. The thought may occur to us that, by carrying the isentropic compression to, or nearly to, point 2-c and reducing the heat supply, an improvement in performance of the Otto engine may be secured. But, in the real engine, line 1-2 represents the compression of the charge, which is a mixture of fuel and air, preliminary to combustion. Point 2 may not be raised above the kindling temperature of the fuel, or a premature explosion will take place, disrupting the cycle.

Let us proceed to a thermodynamic analysis of the Otto air-standard cycle. This is now a heat-engine cycle, and, from Eq. (2:15), its efficiency

$$\eta = \frac{Q_S - Q_R}{Q_S} \quad (2:15)$$

But

$$Q_S = Mc_v(T_3 - T_2)$$

and

$$Q_R = Mc_v(T_4 - T_1)$$

where  $M$  is the mass of the air charge and the notation is that of Figs. 12:2 and 12:3.

Thus

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{Mc_v(T_3 - T_2) - Mc_v(T_4 - T_1)}{Mc_v(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (12:1)$$

From Fig. 12:2,  $V_2 = V_3$ , and  $V_1 = V_4$ , and, based on Eq. (9:40),

$$\frac{T_1}{T_2} = \left( \frac{V_2}{V_1} \right)^{k-1} = \left( \frac{V_3}{V_4} \right)^{k-1} = \frac{T_4}{T_3}$$

which may be expressed in the form

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} = c$$



where  $c$  is a proportionality constant. In terms of this constant, Eq. (12:1) becomes

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{cT_1 - T_1}{cT_2 - T_2} = 1 - \frac{(c - 1)T_1}{(c - 1)T_2} = 1 - \frac{T_1}{T_2} \quad (12:2)$$

$T_1$  and  $T_2$  are the temperatures at the two ends of a reversible adiabatic (isentropic) process, and, substituting equivalent expressions for  $T_1/T_2$  in terms of pressure and volume [see Eq. (9:40) or Table 9:2], the following may also be written:

$$\eta = 1 - \left( \frac{V_2}{V_1} \right)^{k-1} \quad (12:3)$$

$$\eta = 1 - \left( \frac{p_1}{p_2} \right)^{(k-1)/k} \quad (12:4)$$

The ratio  $V_1/V_2$  is called the *compression ratio* of the engine; in the Otto engine it is equal to the *expansion ratio*  $V_4/V_3$ . It will be noted that the efficiency of the Otto air-standard cycle depends solely on the compression ratio for this cycle and that it increases as the compression ratio increases. Thus the efficiencies of the large and the small Otto air-standard cycles of Fig. 12:3 are identical; for process 1-2 is the same for both cycles and represents the same compression ratio. In practice, the compression ratio is limited by the ignition characteristics of the fuel used, as has been explained above. Fuels must be gases, or liquids that can be vaporized for introduction into the air stream in the carburetor. Much progress has been made in the improvement of such fuels so that the ignition of the mixture will not take place until higher temperatures are attained, thus making the use of higher compression ratios, with correspondingly higher efficiencies, possible. This research in fuels has been directed by the result of analyses of the type carried out above and serves as an example of the manner in which thermodynamics may be applied to guide development. Originally, compression ratios of 5 were considered high; with the present selection of fuels, compression ratios above 8 may be used. The ability of a fuel to delay its ignition until higher temperatures are reached is expressed in terms of its *octane number*, higher octane numbers corresponding to higher kindling temperatures. Little or no gain in efficiency results when a fuel of higher octane number than is required to prevent premature ignition is used in an engine of low compression ratio; the octane number has no necessary relation to the heat of reaction of the fuel, but the higher octane fuels are usually more expensive.

The ratio of the volume  $V_2$  to the volume  $V_1 - V_2$  swept through by the piston (the *piston displacement*) is known as the clearance of the engine; thus

$$\text{Clearance} = \frac{V_2}{V_1 - V_2} \quad (12:5)$$

in which the clearance is expressed as a decimal fraction. The clearance is directly dependent upon, and follows from, the compression ratio.

The Otto-cycle engine cylinder combines the function of a compressor with that of an engine, the net output per cycle being the difference between the work performed on the piston during the expansion stroke and the (negative) work of compression. This net work is usually expressed in terms of the *mean effective pressure* (mep), which is the average height of the pressure-volume diagram. The mep is an index to the size of cylinder required for a given net work output per cycle. The size is often a critical factor in the selection of a suitable type of prime mover.

The mep of the air-standard cycle may be calculated by dividing its area, as plotted on pressure-volume coordinates, by the length of the cycle; or since the area of this reversible cycle is the net work of the cycle and is, in turn, equal to the net heat flow,

$$\text{mep} = \frac{W}{V_1 - V_2} = \frac{W}{V_D} = \frac{J(Q_S - Q_R)}{V_D} \quad (12:6)$$

where  $V_D$  is the piston displacement. The terms *indicated* mean effective pressure (imep) and *brake* mean effective pressure (bmep) are both used in connection with the real engine. The imep is obtained by dividing the area of an actual indicator diagram by the length of the diagram, which amounts to dividing the net work performed *on the piston* by the piston displacement. In calculating the bmep, the net work *delivered* by the engine is divided by the piston displacement; the bmep is less than the imep because of the frictional losses in the engine.

*Example 12:3.* An Otto air-standard cycle has a compression ratio of 7. The lowest and highest temperatures of the cycle are 90 and 3000°F, respectively. The pressure at the beginning of compression is 14 psia. Calculate (a) the pressures and temperatures at the key points of the cycle, (b) the heat supplied, the heat rejected, and the net work per pound of air per cycle, (c) the efficiency, (d) the clearance, and (e) the mep of the cycle.

*Solution:*

(a) From data:  $p_1 = 14$  psia;  $T_1 = 550^\circ\text{R}$ ;  $T_3 = 3460^\circ\text{R}$ .

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{k-1} = (550)(7)^{0.4} = (550)(2.18) = 1200^\circ\text{R}$$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^k = (14)(7)^{1.4} = (14)(15.2) = 213 \text{ psia}$$

$$p_3 = p_2 \left( \frac{T_3}{T_2} \right) = 213 \frac{3460}{1200} = 615 \text{ psia}$$

$$T_4 = T_3 \left( \frac{V_3}{V_4} \right)^{k-1} = 3460 \left( \frac{1}{7} \right)^{0.4} = 3460 \left( \frac{1}{2.18} \right) = 1590^\circ\text{R}$$

$$p_4 = p_3 \left( \frac{V_3}{V_4} \right)^k = 615 \left( \frac{1}{7} \right)^{1.4} = 615 \left( \frac{1}{15.2} \right) = 40.5 \text{ psia}$$



$$\begin{aligned}
 (b) \quad Q_S &= Mc_v(T_3 - T_2) = 0.171(3460 - 1200) = 386 \text{ Btu/lb per cycle} \\
 Q_R &= Mc_v(T_4 - T_1) = 0.171(1590 - 550) = 178 \text{ Btu/lb per cycle} \\
 W/J &= Q_S - Q_R = 386 - 178 = 208 \text{ Btu/lb, or } 162,000 \text{ ft-lb/lb per cycle}
 \end{aligned}$$

$$(c) \quad \eta = 1 - \left( \frac{V_2}{V_1} \right)^{k-1} = 1 - \left( \frac{1}{7} \right)^{0.4} = 1 - 0.46 = 0.54$$

Checking,

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{386 - 178}{386} = 0.54$$

$$(d) \quad v_1 = \frac{RT_1}{P_1} = \frac{(53.3)(550)}{(14)(144)} = 14.5 \text{ ft}^3/\text{lb}; \quad v_2 = \frac{14.5}{7} = 2.07 \text{ ft}^3/\text{lb}$$

$$V_D = v_1 - v_2 = 14.5 - 2.07 = 12.43 \text{ ft}^3/\text{lb}$$

$$\text{Clearance} = \frac{V_2}{V_D} = \frac{2.07}{12.43} = 0.166, \text{ or } 16.6 \text{ per cent}$$

$$(e) \quad \text{mep} = \frac{W}{V_D} = \frac{162,000}{(12.43)(144)} = 90.5 \text{ psi}$$

**12:4. The Diesel Cycle.** In 1893 Dr. Rudolf Diesel, recognizing the desirability of supplying heat to the cycle of an internal-combustion engine at as high an average temperature as possible and the handicap incurred in this respect by the Otto engine, due to its compression of a combustible mixture, proposed an engine which would compress a charge consisting of air alone to high temperatures. When the compression stroke had been completed, the fuel was to be injected into the cylinder and to burn progressively as it came in contact with the charge of air; because of the high temperature of the compressed charge, no spark or other ignition system would be required.

Dr. Diesel's original idea was to carry the compression to a temperature as high as could be safely used within the cylinder and then to control the rate of fuel injection, as the piston started on its power stroke, so that the combustion would take place isothermally; a constant-temperature source, as in the Carnot engine, would thus be simulated. He also hoped to approach isothermal rejection of heat at a later point in the cycle by injecting water into the working fluid. Dr. Diesel soon found these isothermal processes to be impractical, but, from his proposal, the form of a present-day cycle that has come to be known as the diesel cycle has been derived. The diesel cycle, as we know it, retains his concept of a high compression of a charge consisting of air alone and the injection of the fuel into the cylinder at a controlled rate during the first part of the power stroke; the rate of fuel injection, however, is calculated to give constant-pressure, rather than constant-temperature, combustion. The other processes of the Otto cycle are retained.

The diesel engine is diagramed in Fig. 12:4. In this engine, the charge drawn into the cylinder is air alone, and a carburetor is not used. No ignition system is required, since the temperature of the charge after com-

pression is high enough to ensure ignition of the fuel as it enters the cylinder; instead, a fuel-injection system is substituted, capable of raising the pressure of the fuel high enough so that the fuel not only can enter the cylinder against the pressure of the compressed charge but also will be thoroughly atomized as it enters. A much less restricted choice in the

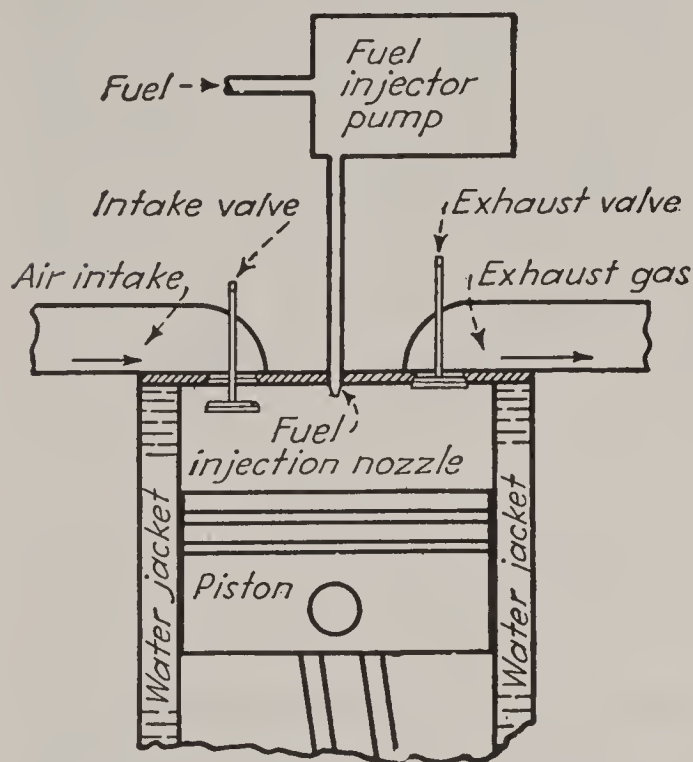


FIG. 12:4. Internal-combustion engine—diesel cycle.

matter of the type of fuel to be used is available than for the Otto-cycle engine, since the fuel need not be volatile; cheaper fuels may therefore be utilized.

The fuel-injection system consists essentially of a fuel-injection pump, driven from the engine shaft, and a fuel-injection nozzle, designed to atomize the fuel thoroughly as it enters the cylinder of the engine. The fuel burns progressively as it enters and comes in contact with the heated air in the cylinder. The rate of fuel delivery must be very carefully proportioned to the change of volume of the charge as

the piston begins its power stroke if the pressure is to remain even approximately constant during the period of combustion. Governing is effected by designing the fuel-injection system so that the time period over which injection takes place can be varied either manually or automatically.

The intake and exhaust valves and the valve-operating mechanism of the diesel engine may be quite similar to Otto-cycle engine practice. The compression ratio is no longer limited by the kindling temperature of the fuel, but only by the practical limits of pressure and temperature that the cylinder can withstand. Indeed, the limit on compression ratio now becomes a lower limit, since the temperature of the compressed charge of air is relied upon to ignite the fuel as it enters the cylinder. Compression ratios used in practice are about 15:1.

When the operations comprising the cycle of a real diesel engine are idealized in the form of the equivalent air-standard cycle, they appear as illustrated on  $PV$  and  $TS$  coordinates in Fig. 12:5. With reference to this figure, the successive processes may be itemized as follows:

1. The adiabatic compression of a charge of air to a high pressure and temperature, represented by the line 1-2.
2. The supply of heat at a rate sufficient to maintain a constant pressure (equivalent to the progressive injection and burning of the fuel in the real engine) during the early part of the power stroke, represented by line 2-3. At point 3 this heat supply ceases.



3. Isentropic expansion of the air charge to the end of the power stroke, 3-4.

4. Rejection of heat from the charge, 4-1, lowering the pressure at constant volume, and preparing the charge for a retraversal of the cycle.

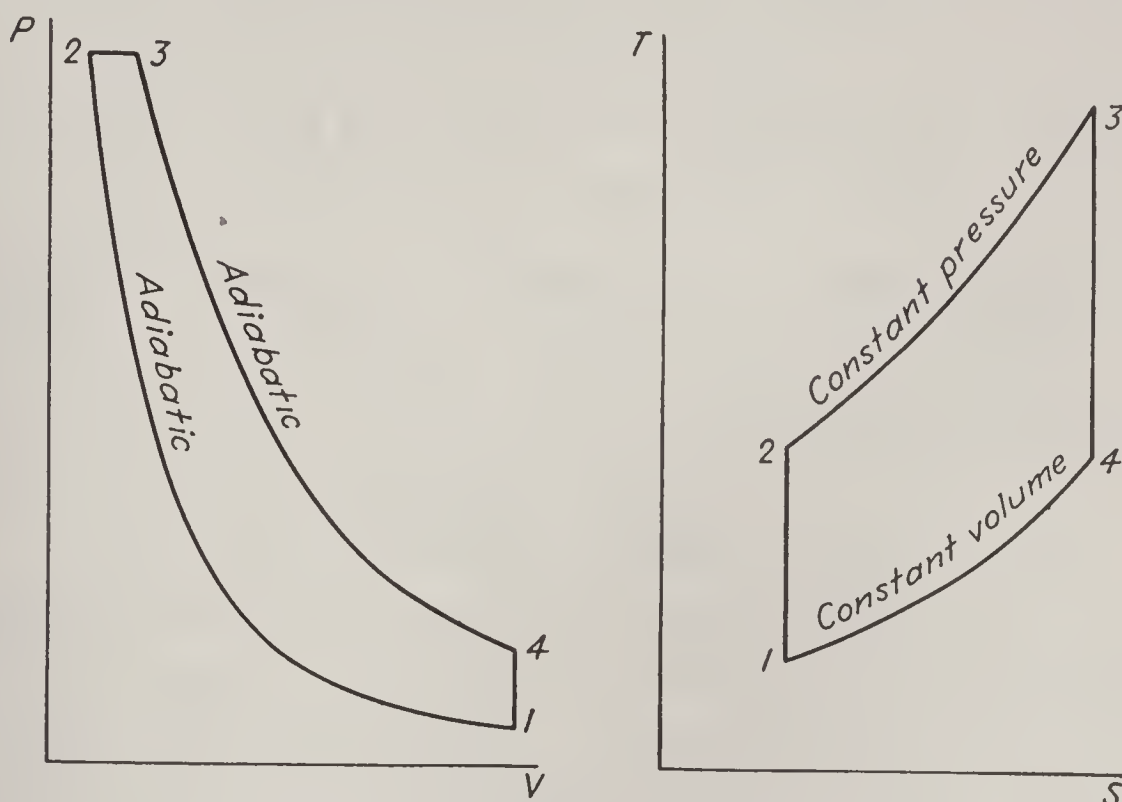


FIG. 12:5. Diesel air-standard cycle.

(This is equivalent to the rejection of the charge of burned gases in the real engine.)

The efficiency of the air-standard diesel cycle may be calculated as below:

$$\begin{aligned} Q_S &= Mc_p(T_3 - T_2) & Q_R &= Mc_v(T_4 - T_1) \\ \eta &= \frac{Q_S - Q_R}{Q_S} = \frac{Mc_p(T_3 - T_2) - Mc_v(T_4 - T_1)}{Mc_p(T_3 - T_2)} \\ &= 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} \quad (12:7) \end{aligned}$$

The temperatures  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$  for substitution in Eq. 12:7 may be found, for a specific cycle, by an application of the information tabulated in Table 9:2. The same definitions of compression ratio, clearance, piston displacement, and mep apply as for the Otto cycle. The expansion ratio  $V_4/V_3$  is smaller than the compression ratio and can be altered independently of the compression ratio by shortening or lengthening the time during which heat is supplied and thus moving point 3 to the left or right. The efficiency, as expressed in Eq. (12:7), is thus evidently not alone a function of the compression ratio for this cycle. The position of point 3, in terms of the *cutoff* percentage, is expressed as

$$\text{Cutoff, per cent} = \frac{V_3 - V_2}{V_1 - V_2} (100) \quad (12:8)$$

The effect of a variation in the percentage of cutoff on the efficiency of the diesel air-standard cycle may be shown as follows:

$$\eta = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} = 1 - \left(\frac{T_1}{T_2}\right) \frac{T_4/T_1 - 1}{k(T_3/T_2 - 1)} \quad (12:9)$$

But

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} \quad T_4 = T_3 \left(\frac{V_3}{V_4}\right)^{k-1} \quad T_1 = T_2 \left(\frac{V_2}{V_1}\right)^{k-1} \quad V_4 = V_1$$

and

$$\frac{T_4}{T_1} = \frac{T_3(V_3/V_4)^{k-1}}{T_2(V_2/V_1)^{k-1}} = \frac{V_3}{V_2} \left(\frac{V_3/V_1}{V_2/V_1}\right)^{k-1} = \frac{V_3}{V_2} \left(\frac{V_3}{V_2}\right)^{k-1} = \left(\frac{V_3}{V_2}\right)^k$$

Substituting these values in Eq. (12:9),

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{k-1} \frac{(V_3/V_2)^k - 1}{k(V_3/V_2 - 1)} \quad (12:10)$$

The ratio  $V_3/V_2$  is unity for zero percentage of cutoff and increases as the cutoff lengthens; it may be called the load ratio. The ratio  $V_2/V_1$  is the reciprocal of the compression ratio. Examination of Eq. (12:10) indicates that the efficiency of the air-standard diesel cycle is a function of both the compression ratio and the percentage of cutoff, or load ratio. A comparison of Eq. (12:10) with Eq. (12:3) indicates that the expression for the efficiency of the air-standard diesel cycle closely resembles that which gives the efficiency of the Otto cycle, differing from it only because of the multiplication of the second term of Eq. (12:3) by the load-ratio factor  $\frac{(V_3/V_2)^k - 1}{k(V_3/V_2 - 1)}$  in Eq. (12:10). As the load ratio approaches unity (*i.e.*, as the cutoff approaches zero), the load-ratio factor approaches 1 as a limit and the efficiency of the air-standard diesel equals that of the air-standard Otto cycle. As the load ratio increases (the cutoff lengthens), the load-ratio factor increases above 1 and the diesel-cycle efficiency is less than the efficiency of an Otto cycle *of the same compression ratio*. This comparison is not fair to the diesel cycle since, as a real engine, it can make use of much higher compression ratios than can the real Otto-cycle engine. A more equitable basis of comparison would be to assume that the maximum temperatures reached in the two cycles were the same; as will be shown later, when this stipulation is made the diesel has the higher efficiency.

*Example 12:4.* A diesel air-standard cycle has a compression ratio of 15. The lowest and highest temperatures of the cycle are 90 and 3000°F, respectively. The pressure at the beginning of compression is 14 psia. Calculate (a) the pressures and temperatures at the key points of the cycle, (b) the heat supplied, heat rejected, and net work per pound of air per cycle, (c) the efficiency, (d) the clearance in per cent. (e) the mep of the cycle, and (f) the cutoff percentage.



*Solution:*

(a) From data:  $p_1 = 14$  psia;  $T_1 = 550^\circ\text{R}$ ;  $T_3 = 3460^\circ\text{R}$ .

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{k-1} = (550)(15)^{0.4} = (550)(2.96) = 1630^\circ\text{R}$$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^k = (14)(15)^{1.4} = (14)(44.5) = 623 \text{ psia} = p_3$$

$$\frac{V_3}{V_2} = \frac{T_3}{T_2} = \frac{3460}{1630} = 2.12; \frac{V_3}{V_4} = \frac{V_3}{V_1} = \frac{V_3}{V_2} \frac{V_2}{V_1} = 2.12 \left( \frac{1}{15} \right) = 0.141$$

$$T_4 = T_3 \left( \frac{V_3}{V_4} \right)^{k-1} = (3460)(0.141)^{0.4} = (3460)(0.457) = 1580^\circ\text{R}$$

$$p_4 = p_3 \left( \frac{V_3}{V_4} \right)^k = (623)(0.141)^{1.4} = (623)(0.064) = 40 \text{ psia}$$

(b)  $Q_S = Mc_p(T_3 - T_2) = 0.24(3460 - 1630) = 439$  Btu/lb per cycle

$$Q_R = Mc_v(T_4 - T_1) = 0.171(1580 - 550) = 176 \text{ Btu/lb per cycle}$$

$$W/J = Q_S - Q_R = 439 - 176 = 263 \text{ Btu/lb, or } 205,000 \text{ ft-lb/lb per cycle}$$

$$(c) \eta = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} = 1 - \frac{1580 - 550}{1.4(3460 - 1630)} = 1 - 0.402 = 0.598$$

Checking,

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{439 - 176}{439} = 0.598$$

or, using Eq. (12:10),

$$\eta = 1 - \left( \frac{1}{15} \right)^{0.4} \frac{2.12^{1.4} - 1}{1.4(2.12 - 1)} = 1 - 0.338 \left( \frac{1.86}{1.57} \right) = 0.598$$

Note that the efficiency of an Otto cycle of this compression ratio is  $1 - \left( \frac{1}{15} \right)^{0.4} = 0.662$ .

(d)  $v_1 = 14.5 \text{ ft}^3/\text{lb}$  [Ex. 12:3];  $v_2 = v_1/15 = 14.5/15 = 0.966 \text{ ft}^3/\text{lb}$

$$V_D = v_1 - v_2 = 14.5 - 0.966 = 13.53 \text{ ft}^3/\text{lb}$$

$$\text{Clearance} = \frac{v_2}{V_D} = \frac{0.966}{13.53} = 0.0713, \text{ or } 7.13 \text{ per cent}$$

$$(e) \text{ mep} = \frac{W}{V_D} = \frac{205,000}{(13.53)(144)} = 105 \text{ psi}$$

$$(f) v_3 = \frac{V_3}{V_2} v_2 = (2.12)(0.966) = 2.145$$

$$\text{Cutoff, per cent} = \frac{(v_3 - v_2)(100)}{V_D} = \frac{(2.145 - 0.966)(100)}{13.53} = 8.7 \text{ per cent}$$

**12:5. The Dual Cycle.** Originally, the atomization of the fuel as it entered the cylinder of the diesel engine was assisted by introducing it in a stream of secondary air at high pressure; the expansion of this jet of air as it entered the cylinder caused the fuel jet to be shattered into minute particles and to spread through the combustion space. The tendency in diesel design has been toward the elimination of this secondary air supply, so that the fuel alone is injected into the cylinder and dependence is placed on a high pressure differential across the fuel-injection nozzle for proper

atomization. This has led to a variant of the diesel cycle, called the dual (for dual-combustion) cycle; it is illustrated in Fig. 12:6 on  $PV$  and  $TS$  coordinates. The real engine that operates on an approximation of this cycle differs little in its construction from the diesel of Fig. 12:4, except that the compression ratio is usually somewhat smaller. The cycle of operation is slightly changed by advancing the time at which fuel first enters the cylinder, and the first part of the fuel charge is introduced while the piston is practically stationary; as a result, the first part of the com-

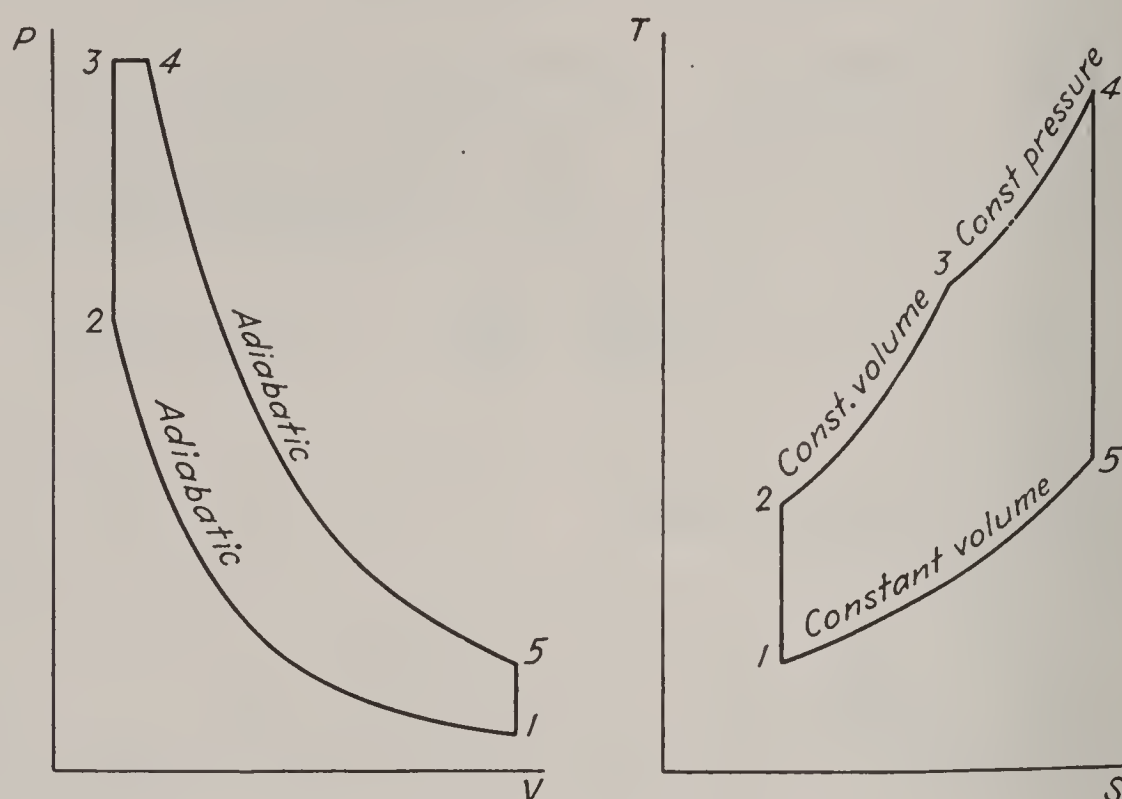


FIG. 12:6. Dual air-standard cycle.

bustion takes place at nearly constant volume. The balance of the fuel is injected during the early part of the power stroke, as in the diesel cycle, and the rest of the cycle is the same as the diesel cycle. To distinguish them from the true diesel, engines based on the dual cycle are called compression-ignition (CI) engines. They retain the advantages of the diesel in permitting a wider selection of fuels and higher compression ratio than are available to the real Otto-cycle engine. It may be shown that, *on the basis of the same compression ratio*, the efficiency of the air-standard dual cycle is less than that of the Otto, but greater than that of the diesel. On the more practical basis of comparing the efficiencies of these cycles when the maximum temperature reached as the result of combustion is the same for each, the diesel enjoys a slight advantage over the dual cycle, but the latter is superior to the Otto. It is suggested that the reader derive an expression for the efficiency of the air-standard dual cycle in terms of the temperatures at the key points around the cycle of Fig. 12:6 and examine that expression with a view to determining what factors control the efficiency.



**Example 12:5.** A dual-combustion air-standard cycle has a compression ratio of 10. The constant-pressure part of the combustion takes place at a pressure of 623 psia. The lowest and highest temperatures of the cycle are 90 and 3000°F, respectively. The pressure at the beginning of compression is 14 psia. Calculate (a) the pressures and temperatures at the key points of the cycle, (b) the heat supplied at constant volume and at constant pressure, the heat rejected, and the net work of the cycle per pound of air, (c) the efficiency, and (d) the mep of the cycle.

*Solution:*

(a) From data:  $p_1 = 14$  psia;  $T_1 = 550^\circ\text{R}$ ;  $p_3 = p_4 = 623$  psia;  $T_4 = 3460^\circ\text{R}$ .

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{k-1} = (550)(10)^{0.4} = (550)(2.51) = 1380^\circ\text{R}$$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^k = (14)(10)^{1.4} = (14)(25.0) = 350 \text{ psia}$$

$$T_3 = T_2 \frac{p_3}{p_2} = 1380 \left( \frac{623}{350} \right) = 2460^\circ\text{R}$$

$$\frac{V_4}{V_3} = \frac{T_4}{T_3} = \frac{3460}{2460} = 1.408 = \frac{V_4}{V_2}; \frac{V_4}{V_5} = \frac{V_4}{V_1} = \frac{V_4}{V_2} \frac{V_2}{V_1} = \frac{1.408}{10} = 0.1408$$

$$T_5 = T_4 \left( \frac{V_4}{V_5} \right)^{k-1} = (3460)(0.1408)^{0.4} = (3460)(0.457) = 1580^\circ\text{R}$$

$$p_5 = p_4 \left( \frac{V_4}{V_5} \right)^k = (623)(0.1408)^{1.4} = (623)(0.064) = 40 \text{ psia}$$

$$(b) (Q_S)_v = Mc_v(T_3 - T_2) = 0.171(2460 - 1380) = 184.5 \text{ Btu/lb}$$

$$(Q_S)_p = Mc_p(T_4 - T_3) = 0.240(3460 - 2460) = 240.0 \text{ Btu/lb.}$$

$$Q_S = 424.5 \text{ Btu/lb}$$

$$Q_R = Mc_v(T_5 - T_1) = 0.171(1580 - 550) = 176 \text{ Btu/lb}$$

$$W/J = Q_S - Q_R = 424.5 - 176 = 248.5 \text{ Btu/lb, or } 193,000 \text{ ft-lb/lb}$$

$$(c) \eta = \frac{Q_S - Q_R}{Q_S} = \frac{248.5}{424.5} = 0.585$$

$$(d) v_1 = 14.5 \text{ ft}^3/\text{lb}; v_2 = 14.5/10 = 1.45 \text{ ft}^3/\text{lb}$$

$$\text{mep} = \frac{193,000}{(14.5 - 1.45)(144)} = 102.5 \text{ psi}$$

## 12:6. Comparison of Otto-, Diesel-, and Dual-cycle Efficiencies.

Some attention has been given in preceding paragraphs to the comparison of the efficiencies of the Otto, diesel, and dual air-standard cycles. In Chap. 6 it has been pointed out that an excellent tool for the purpose is the temperature-entropy diagram. The comparison of these cycles on that diagram is shown in Fig. 12:7, the basis of the comparison being equality of the highest and lowest temperatures of the cycles (at points  $3_o$ ,  $3_D$ ,  $4_d$ , and point 1, respectively). The outline of the Otto cycle is shown in solid, of the diesel cycle in dashed, and of the dual cycle in dash-dot lines, and the notation corresponds to that of Figs. 12:2, 12:3, 12:5, and 12:6. The subscripts  $O$ ,  $D$ , and  $d$  refer, respectively, to the Otto, the diesel, and the dual cycles. It will be noted that the cycles differ only at their tops, the isentropic expansion lines (3-4 for the Otto and diesel and 4-5 for the dual) and the lines representing the constant-volume rejection of heat

(4-1 for the Otto and diesel and 5-1 for the dual) being the same for each cycle. The compression ratio is represented by the length of the line 1-2 in each cycle and, based upon the premise adopted above, is greatest for the diesel, least for the Otto cycle.

The efficiencies of these reversible cycles may be visually estimated as the ratio of their enclosed areas (their net work) to the area between their top lines (2-3 for the Otto and diesel, 2-3-4 for the dual) and the  $S$  axis,

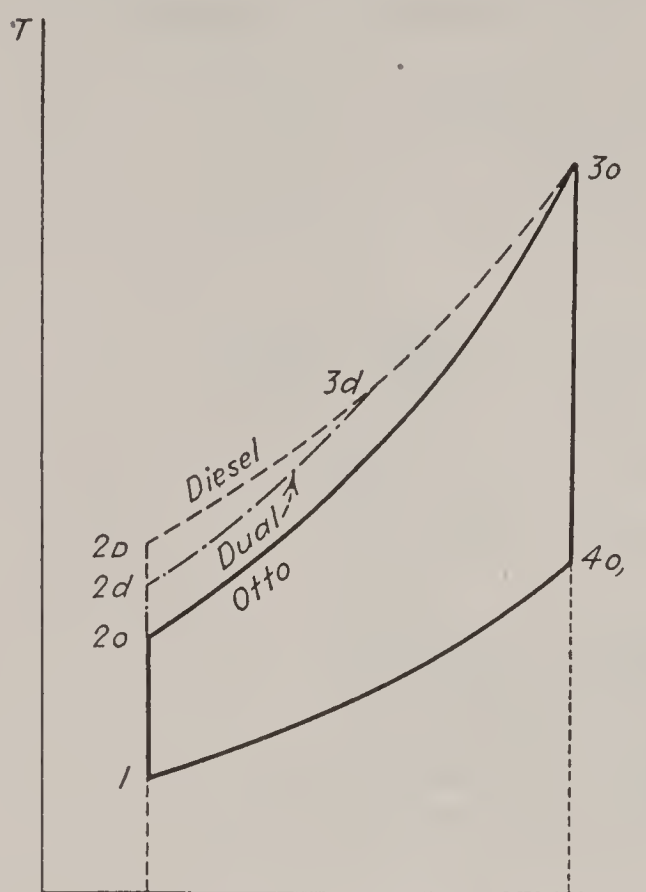


FIG. 12:7. Comparison of Otto, diesel, and dual air-standard cycles.

this area representing the heat supplied by the source; the advantage of the diesel and dual cycles over the Otto cycle is readily apparent. It is suggested that the reader make the same comparison, based on the same premise, between the cycles as they appear on  $PV$  coordinates and note that the same conclusions are not so evident. Also, he may compare them on  $TS$  coordinates, but based on the assumption of equal compression ratios for each cycle, and check the results of his comparison against the equivalent, but more laborious, comparison as made in Arts. 12:4 and 12:5. The purpose is, of course, to emphasize the advantage in the use of the  $TS$  diagram as a tool for comparing the efficiencies of reversible cycles.

**12:7. The Lenoir engine** is of no present-day practical importance. It does have interest for us as the first form in which the internal-combustion engine was built and because it illustrates the way in which a knowledge of thermodynamic principles may guide research and lead to eventual improvement in heat-work apparatus.

The Lenoir engine was a two-stroke-cycle engine, with intake and exhaust valves in the head of the cylinder. As the piston moved away from the head, with the intake valve open and the exhaust valve closed, a charge consisting of a mixture of fuel and air was drawn into the cylinder. Part way in the stroke of the piston, the intake valve was closed, and the charge then within the cylinder was ignited and exploded without previous compression. Because of this explosion, the pressure within the cylinder was raised, and, during the latter part of its stroke, work was performed on the piston as the pressure gradually decreased. At the end of this piston stroke the exhaust valve opened, and the burned gases were expelled during the exhaust stroke of the piston. At the end of this exhaust



stroke, the exhaust valve closed, and the intake valve opened, preparatory to retracing the cycle. The cycle, idealized in the form of an approximately equivalent air-standard cycle, is shown in Fig. 12:8. The actual cycle differed widely from this idealization, both because the rapid movement of the piston at the time of explosion made the combustion line 2-3 vary greatly from the vertical rise of pressure pictured in the figure and because the pressure at the end of the power stroke did not necessarily correspond to the pressure at which the charge was inducted.

In devising what is now known as the Otto cycle, Beau de Rochas was able to make a long step in the advancement of internal-combustion-engine theory because of his recognition of the thermodynamic principle

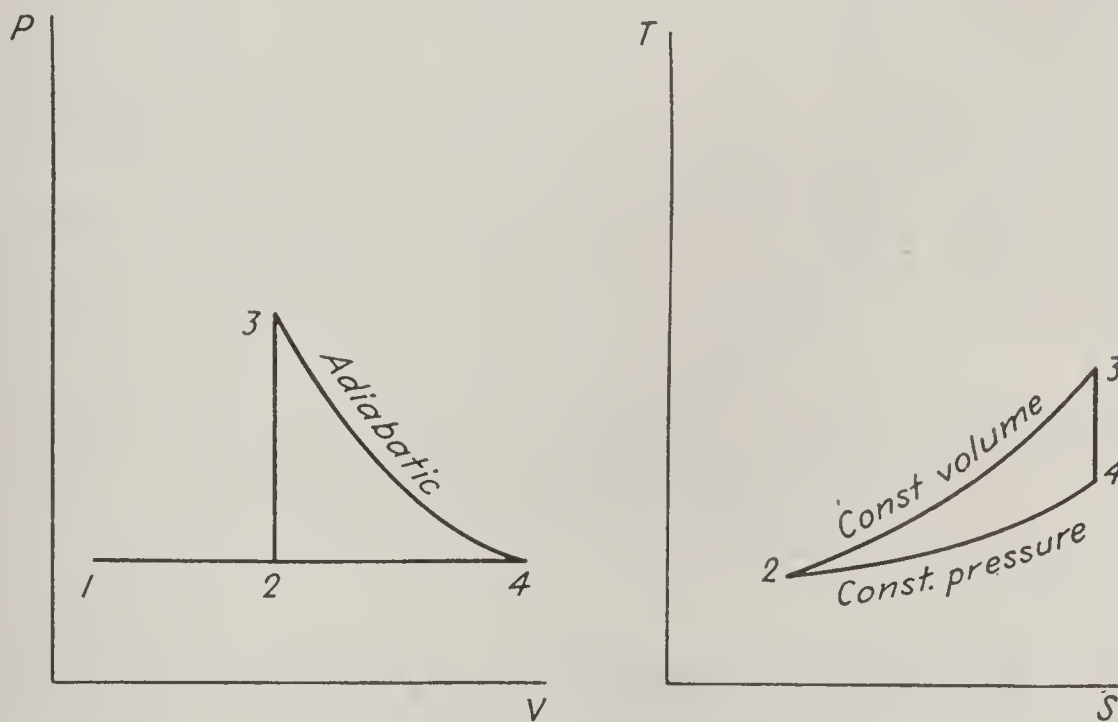


FIG. 12:8. Lenoir air-standard cycle.

that, for high efficiency, heat should be supplied the cycle at as high an average temperature as is practicable. The purpose of the precompression of the charge, which he first introduced, was to raise this average temperature, and, since his day, precompression of the charge has been accepted as a basic principle to be applied in internal-combustion-engine design. It is suggested that the reader both derive an expression for the efficiency of the Lenoir air-standard cycle of Fig. 12:8 and make a comparison on  $TS$  coordinates, in the manner of Fig. 12:7, with cycles that employ precompression.

**12:8. The Brayton (Gas-turbine) Cycle.** If the adiabatic expansion line 3-4 of the  $PV$  diagram of Fig. 12:5 is prolonged until the pressure at point 1 of the cycle is reached, it is evident that an extra dividend of work will be obtained, equal to the toe-shaped area which is added when the end of this extended process is connected to point 1 of the cycle by a constant-pressure line. Moreover, this extra work of the cycle does not come at the expense of any increase in heat supplied the cycle, since the heat-

supply line 2-3 need not change its position nor its length. The resulting cycle is known as the *Brayton air-standard cycle* and is the basic cycle underlying the operation of the gas-turbine power plant. The Brayton air-standard cycle is shown on  $PV$  and  $TS$  coordinates in Fig. 12:9. The improvement in efficiency over the diesel is shown even more clearly by comparing the  $TS$  diagrams of Figs. 12:5 and 12:9. This comparison

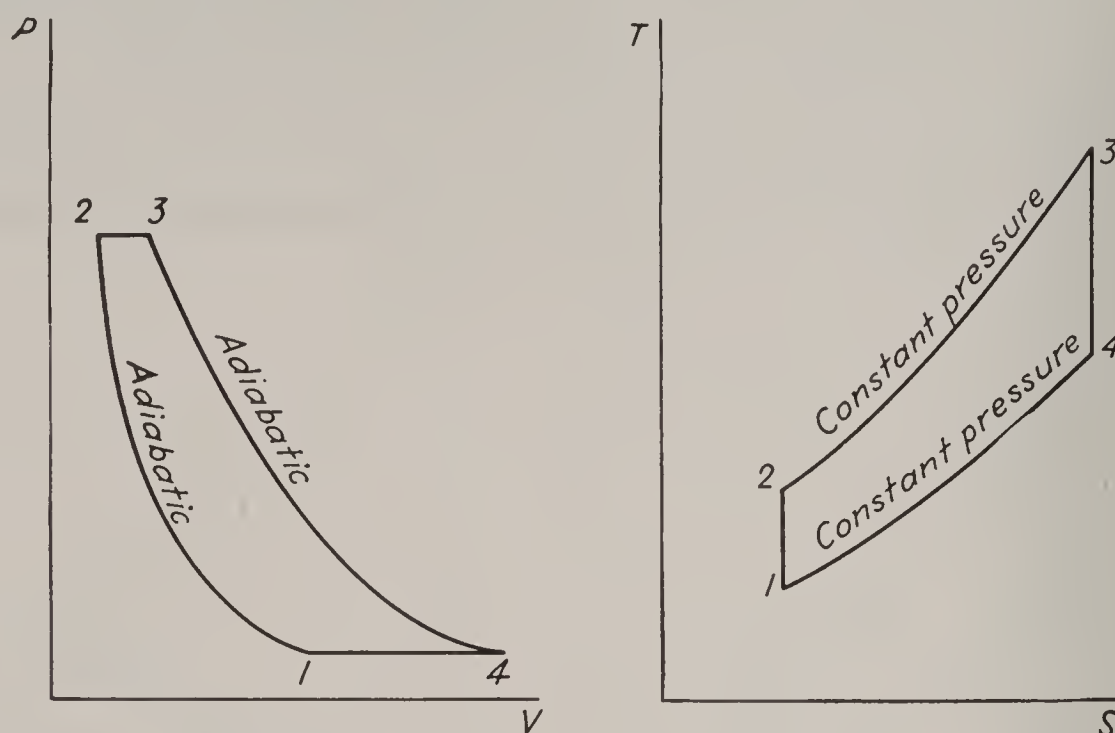


FIG. 12:9. Brayton air-standard cycle.

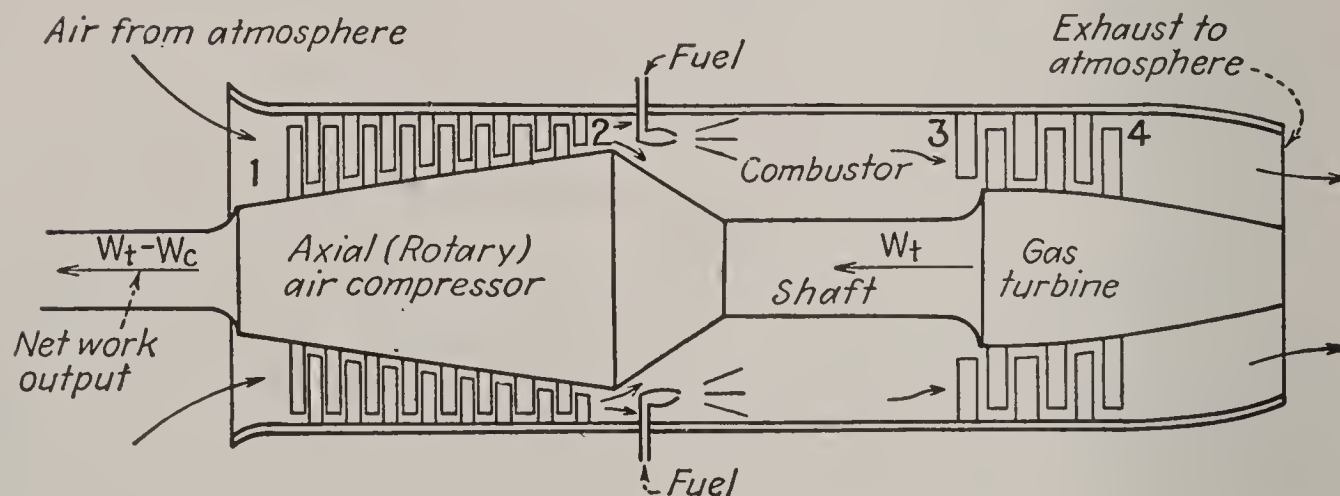


FIG. 12:10. Schematic diagram of gas-turbine power plant.

shows that the increase in net work results from a reduction in the amount of heat discharged to the refrigerator.

The Otto, diesel, and compression-ignition power plants are typically built in the form of reciprocating engines, but the real power plant that is based on the Brayton cycle is a steady-flow device consisting of an air compressor and a gas turbine in series. Fuel is burned in the air as it leaves the compressor and still further increases its temperature and thus its volume as it enters the gas turbine for reexpansion to atmospheric pressure. A schematic diagram of the elements of the gas-turbine power plant is presented in Fig. 12:10. It is evident that the work required to



drive the compressor is a charge against, and must be deducted from, the work delivered by the turbine in arriving at the net work of the entire plant. In Fig. 12:11, the work expended on compression is proportional to the area 1-2-b-a, while the work of the turbine is represented by the area b-3-4-a. The net work of the cycle is therefore proportional to the area 1-2-3-4, which is, of course, the Brayton cycle. Since the gas-turbine power plant is a steady-flow device, the volumes as shown in this figure would conveniently be based on a unit mass of the fluid. In converting to the air-standard basis for convenient thermodynamic analysis, the only change that is necessary is to substitute a simple addition of heat sufficient to produce the change of temperature and specific volume between points 2 and 3 and a rejection of enough heat, between points 4 and 1, to change an air system of unit mass between those states.

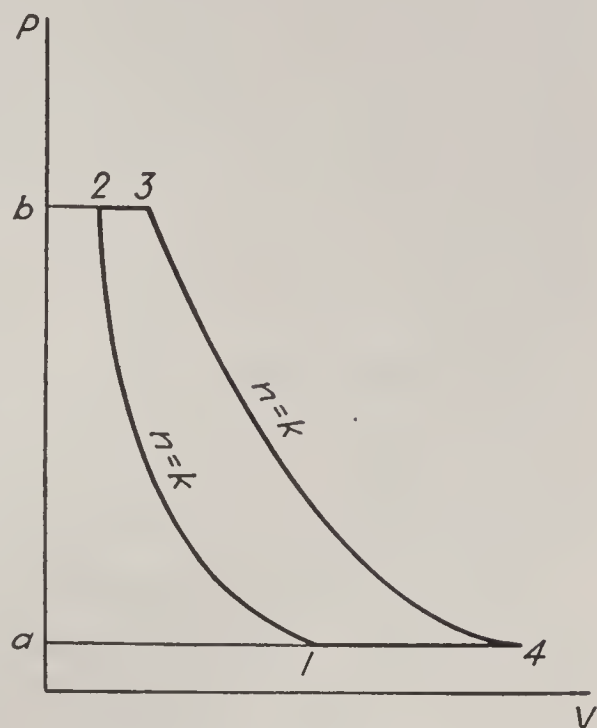


FIG. 12:11. Work areas—Brayton cycle.

As an air-standard cycle, the Brayton cycle may be analyzed, as below:

$$Q_S = c_p(T_3 - T_2) \quad Q_R = c_p(T_4 - T_1)$$

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{c_p(T_3 - T_2) - c_p(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} = \left(\frac{p_3}{p_4}\right)^{(k-1)/k} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2} = c$$

(proportionality const)

Then

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{cT_1 - T_1}{cT_2 - T_2} = 1 - \frac{(c-1)T_1}{(c-1)T_2} = 1 - \frac{T_1}{T_2} \quad (12:11)$$

Comparing this expression with Eq. (12:2), the efficiency of the air-standard Brayton cycle is found to be identical with that of the air-standard Otto and to be dependent only on the compression ratio. However, as a steady-flow device, the compression ratio of the axial-flow compressor is better expressed in terms of the limiting pressures, rather than the limiting volumes, and, since  $T_1/T_2 = (p_1/p_2)^{(k-1)/k}$ , we may write

$$\eta = 1 - \left(\frac{p_1}{p_2}\right)^{(k-1)/k} \quad (12:12)$$

The possibilities of the Brayton cycle, translated into the practical form

of the gas-turbine power plant, seem to be tremendous. Not only does the air-standard cycle equal in efficiency the efficiency of the air-standard Otto, but the gas-turbine power plant is not limited to low compression ratios, since the compressor handles air alone and not a combustible mixture; nor is volatility a necessary property of the fuel, and a selection may be made from a wider range of fuels. What is perhaps an even more important advantage is based on the limited power which the reciprocating internal-combustion engine may develop. Because the intermittent character of the flow of the working fluid through them limits the mass of working fluid which they can accept, Otto, diesel, and compression-ignition engines are bulky and expensive and are limited to comparatively low capacities. The gas-turbine power plant, on the other hand, does not suffer from these limitations.

The advantages suggested in the foregoing paragraph have not, at the present time, been fully realized because of practical factors, the most important of which is the metallurgical limit. Progress is being made in the improvement of the gas-turbine power plant along lines such as will be suggested later in our discussion; many of these improvements are based directly on thermodynamic principles. The reciprocating internal-combustion power plant may utilize, by proper design, the maximum temperatures within the cylinder which are available to the engineer as a result of the combustion process. This is possible partly because the piston and internal surfaces of the cylinder are exposed to these temperatures over only a small fraction of the entire cycle; during the balance of the cycle, temperatures are lower, and these parts have an opportunity to pass on the heat which they receive. But the temperature at entry to the turbine of the gas-turbine power plant is steadily maintained; moreover, the cooling of the turbine blades is much less effective than the cooling of an engine piston, and they attain practically the same temperature as the gases which flow over them. At present, metallurgical research has developed blades which can, as an extreme limit, retain necessary strength and resistance to corrosion at temperatures of around  $2000^{\circ}\text{F}$ , and the temperature at entry to the turbine must be held below this level. It will be noted that this temperature is far above the accepted metallurgical limit for the usual materials with which the engineer works.

If the compressor and turbine of the gas-turbine power plant could be built to carry out reversible (isentropic) processes, the limitation in the maximum temperature of the cycle would, as is indicated by Eq. (12:12), have no effect on the efficiency of the cycle. The two Brayton cycles shown in Fig. 12:12, a Mollier diagram, which differ only in the amount of heat supply and, consequently, the temperature of the gas as it flows through the turbine, would thus have the same efficiency. Instead, best present-day practice limits the maximum attainable efficiency of



either compressor or turbine to a maximum of about 85 per cent, and there seems to be little chance for any considerable increase above that level. Indeed, it is only because of comparatively recent improvements in compressor and turbine performance that the gas-turbine power plant has been able to enter into serious competition with the internal-combustion reciprocating engine. The irreversibilities encountered in flow through the compressor and turbine may be shown on the Mollier diagram as a shifting of points 2 and 4 to higher entropies, as was brought out in Chap. 11 and as is illustrated in Fig. 12:12 by the position of points 2' and 4'. Thus the net work of the cycle is  $(h_3 - h_{4'}) - (h_{2'} - h_1)$ , a smaller amount than for the reversible cycle, both because the turbine work is less and because the work of compression is greater than for that cycle. It will be readily appreciated that, if the irreversibilities are serious, it is possible that no net work may be realized. Moreover, this effect is relatively more serious, at given compressor and turbine efficiency, for the smaller cycle of Fig. 12:12 than for the larger, because the elevation of point 2' above point 2 is based not upon the area of the Brayton cycle but upon the work of the compressor, and, similarly, the amount by which  $h_{4'}$  is greater than  $h_4$  depends upon the gross work of the turbine. If higher temperatures could be maintained in flow through the turbine, corresponding to the larger cycle of the figure, the loss in the net work of the cycle, in other words, would be relatively less serious and the efficiency of the real gas-turbine power plant would be greater. It would appear that one of the most profitable fields for research toward the improvement of the efficiency of the gas-turbine power plant lies in the development of alloys still more heat-resistant than those at present available.

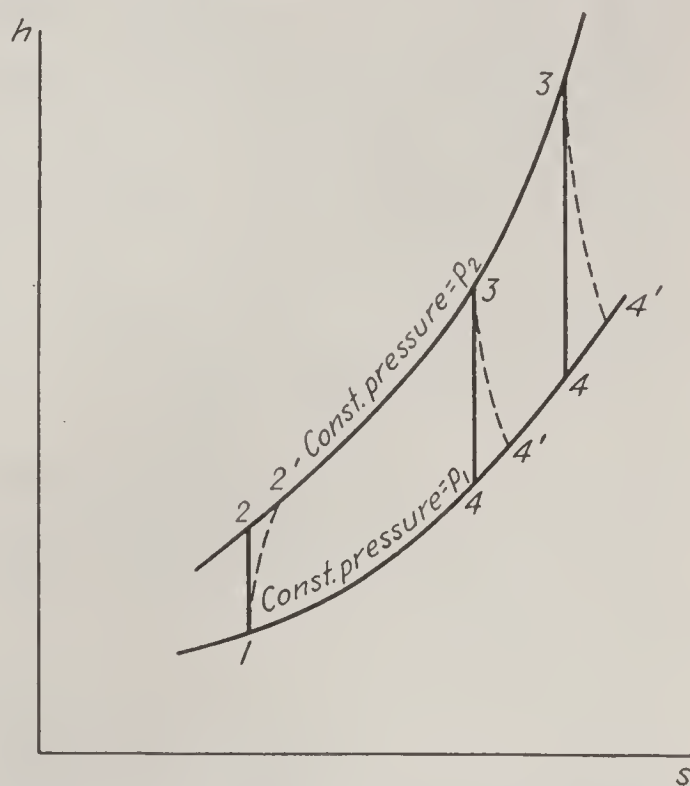


FIG. 12:12. Gas-turbine power-plant cycle—effect of metallurgical limit.

*Example 12:8A.* A Brayton air-standard cycle operates between pressures of 14 and 140 psia, and the lowest and highest temperatures of the cycle are 90 and 3000°F, respectively. Calculate (a) the temperatures at the end of compression and at the end of expansion, (b) the heat supplied, heat rejected, and net work per pound of air, and (c) the efficiency. (d) If the compressor and turbine processes are each assumed to be carried out at 85 per cent efficiency, what is the effect on the efficiency of the cycle?

*Solution:*

(a) From data:  $p_1 = p_4 = 14$  psia;  $p_2 = p_3 = 140$  psia;  $T_1 = 550^\circ\text{R}$ ;  $T_3 = 3460^\circ\text{R}$ .

$$T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{(k-1)/k} = (550)(10)^{0.4/1.4} = (550)(1.93) = 1060^\circ\text{R}$$

$$T_4 = T_1 \frac{T_3}{T_2} = 550 \left( \frac{3460}{1060} \right) = 1790^\circ\text{R}$$

$$(b) Q_S = c_p(T_3 - T_2) = 0.24(3460 - 1060) = 576 \text{ Btu/lb}$$

$$Q_R = c_p(T_4 - T_1) = 0.24(1790 - 550) = 298 \text{ Btu/lb}$$

$$\text{Net work} = Q_S - Q_R = 278 \text{ Btu/lb}$$

$$(c) \eta = 1 - \left( \frac{p_1}{p_2} \right)^{(k-1)/k} = 1 - \left( \frac{1}{10} \right)^{0.4/1.4} = 1 - 0.518 = 0.482$$

Checking,

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{278}{576} = 0.482$$

(d) Based on a compressor efficiency of 0.85 and using the notation of Fig. 12:12,

$$\frac{h_1 - h_2}{h_1 - h_{2'}} = 0.85 \text{ or } \frac{c_p(T_1 - T_2)}{c_p(T_1 - T_{2'})} = \frac{550 - 1060}{550 - T_{2'}} = 0.85 \text{ and } T_{2'} = 1150^\circ\text{R}$$

For the turbine,

$$\frac{h_3 - h_{4'}}{h_3 - h_4} = 0.85 \text{ or } \frac{c_p(T_3 - T_{4'})}{c_p(T_3 - T_4)} = \frac{3460 - T_{4'}}{3460 - 1790} = 0.85 \text{ and } T_{4'} = 2040^\circ\text{R}$$

$$\text{Compressor work} = c_p(T_1 - T_{2'}) = 0.24(550 - 1150) = -144 \text{ Btu/lb}$$

$$\text{Turbine work} = c_p(T_3 - T_{4'}) = 0.24(3460 - 2040) = 340 \text{ Btu/lb}$$

$$\text{Net work} = 196 \text{ Btu/lb}$$

$$Q_S = c_p(T_3 - T_{2'}) = 0.24(3460 - 1150) = 554 \text{ Btu/lb}$$

$$\eta = \frac{\text{net work}}{Q_S} = \frac{196}{554} = 0.354$$

The cycle efficiency has been reduced by slightly more than one-fourth by introducing the irreversibilities of the compressor and the turbine into the problem.

*Example 12:8B.* Solve the problem of Example 12:8A, obtaining the same quantities, but based on a maximum temperature of  $2000^\circ\text{F}$  (instead of  $3000^\circ\text{F}$ ).

*Solution:*

(a) From data:  $p_1 = p_4 = 14$  psia;  $T_1 = 550^\circ\text{R}$ ;  $T_3 = 2460^\circ\text{R}$ ;  $T_2 = (550)(10)^{0.4/1.4} = 1060^\circ\text{R}$ ;  $T_4 = T_1 \left( \frac{T_3}{T_2} \right) = 550 \left( \frac{2460}{1060} \right) = 1275^\circ\text{R}$ .

$$(b) Q_S = 0.24(2460 - 1060) = 336 \text{ Btu/lb}$$

$$Q_R = 0.24(1275 - 550) = 174 \text{ Btu/lb}$$

$$\text{Net work} = Q_S - Q_R = 162 \text{ Btu/lb}$$

$$(c) \eta = \frac{Q_S - Q_R}{Q_S} = \frac{162}{336} = 0.482$$

$$(d) \frac{T_1 - T_2}{T_1 - T_{2'}} = \frac{550 - 1060}{550 - T_{2'}} = 0.85 \text{ and } T_{2'} = 1150^\circ\text{R}$$

$$\frac{T_3 - T_{4'}}{T_3 - T_4} = \frac{2460 - T_{4'}}{2460 - 1275} = 0.85 \text{ and } T_{4'} = 1453^\circ\text{R}$$



$$\begin{aligned}
 \text{Compressor work} &= 0.24(550 - 1150) = -144 \text{ Btu/lb} \\
 \text{Turbine work} &= 0.24(2460 - 1453) = 242 \text{ Btu/lb} \\
 \text{Net work} &= 98 \text{ Btu/lb} \\
 Q_s &= 0.24(2460 - 1150) = 315 \text{ Btu/lb} \\
 \eta &= \frac{\text{net work}}{Q_s} = \frac{98}{315} = 0.312
 \end{aligned}$$

Note that the effect on cycle efficiency of including compressor and turbine irreversibilities has been more serious here than in Example 12:8A.

**12:9. Improvements in the Gas-turbine Power-plant Cycle.** While awaiting the products of continuing metallurgical research, there are some steps that can, and are, being taken with a view toward increasing the efficiency of the gas-turbine power plant. Essentially, these consist of various applications of the principle of regeneration. The gas-turbine power plant, as a steady-flow device, is well adapted for the employment

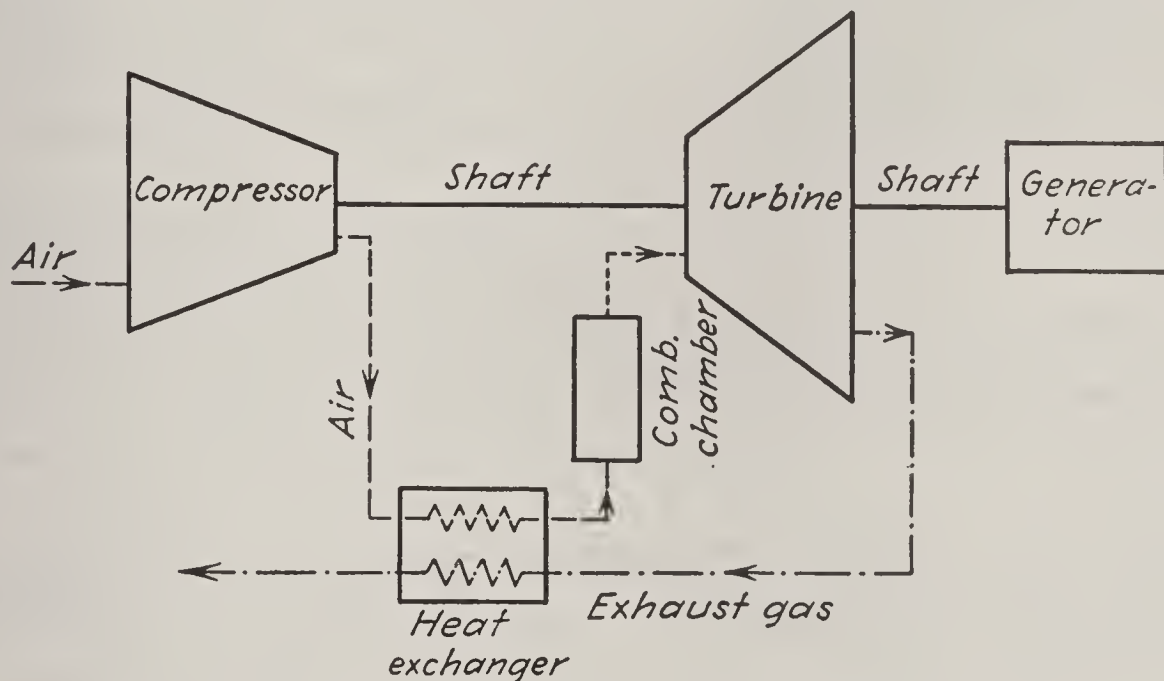


FIG. 12:13. Regeneration in the gas-turbine power plant.

of regeneration without the necessity of including complicated heat exchangers of the type described in Art. 4:6. The temperature at point 4 of the Brayton cycle is often above that at point 2. In the gas-turbine power plant, these points represent, respectively, the states of the fluid as exhausted from the turbine and as discharged from the compressor; the thought occurs that some of the fuel can be saved by utilizing the stored energy in the exhaust gases to preheat the air before it enters the combustion chamber. Note that this preheating should be done after, rather than before, compression, or the work of compression will be increased. The flow arrangement is diagramed in Fig. 12:13. In the limit never reached in practice, the use of counterflow heat exchange, as shown in the figure, would permit the compressed air to be raised in temperature to  $T_4$ , while the turbine exhaust cools to  $T_2$ . The effect upon the air-standard cycle is shown in Fig. 12:14, where the crosshatched

areas are equal and represent the heat exchanged. The net work of the air-standard cycle is not affected, but the heat supplied *from the source* is reduced in the proportion  $(T_3 - T_4)/(T_3 - T_2)$ , with a consequent improvement in cycle efficiency.

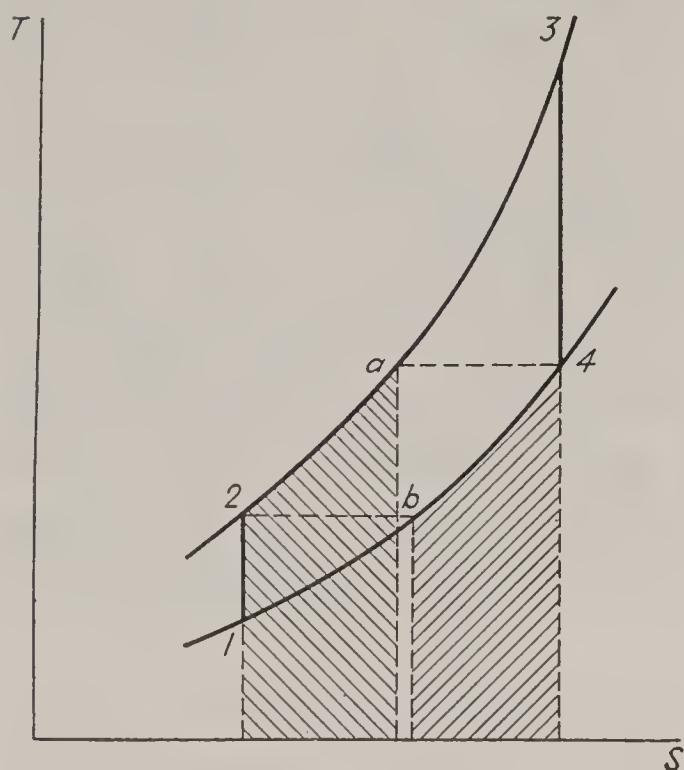


FIG. 12:14. Brayton cycle—effect of regeneration.

*Example 12:9A.* Apply regeneration to the cycle of Example 12:8B, part d, and show the effect on the efficiency of the cycle. Assume regeneration to be ideal, i.e., the air enters the combustion chamber at the temperature  $T_4'$ .

*Solution.* This would have no effect on the compressor or turbine work. The heat supplied would be reduced to

$$Q_s = c_p(T_3 - T_4') = 0.24(2460 - 1453) = 242 \text{ Btu/lb}$$

$$\eta = \frac{\text{net work}}{Q_s} = \frac{98}{242} = 0.405$$

Other steps that may be taken toward the attainment of higher efficiencies of the gas-turbine power plant include the compression of the air in two (or more) compressors in series, with intercooling of the air between

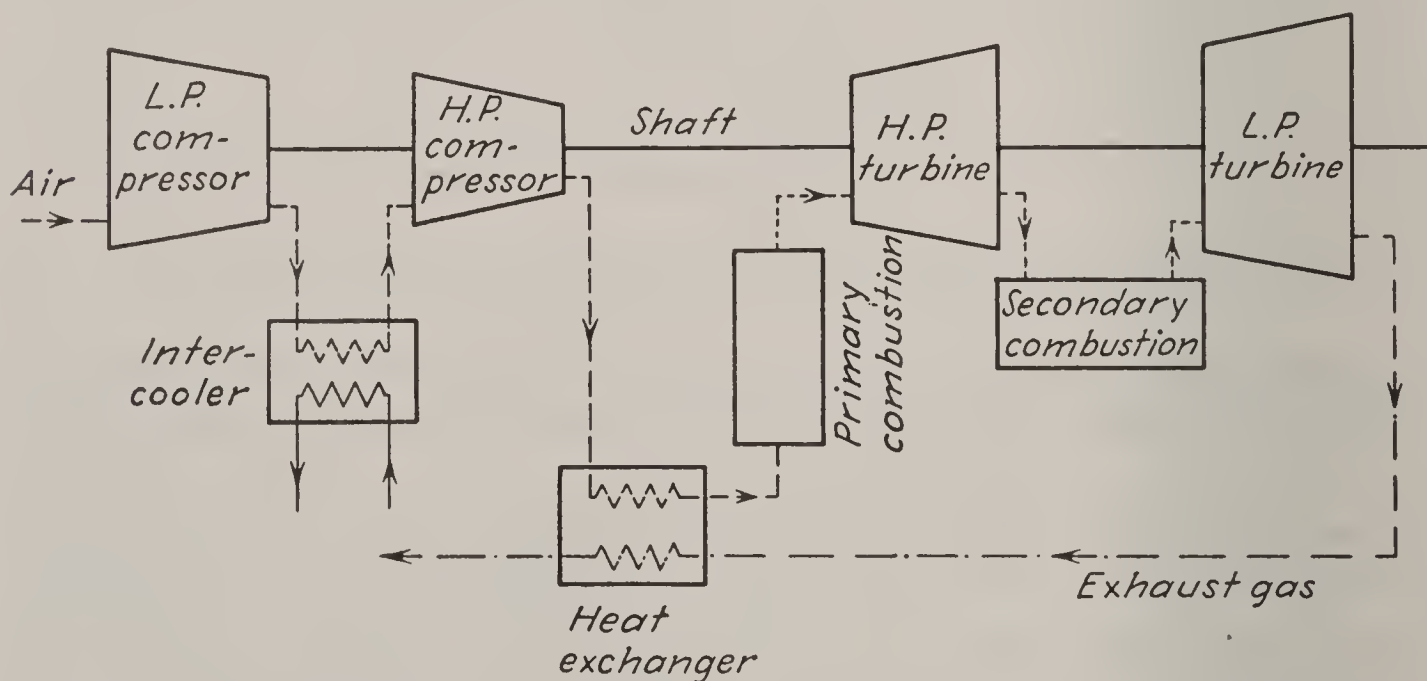


FIG. 12:15. The gas-turbine power plant—staged compression and expansion.

compression steps, and the similar division of the expansion into two steps, the gases being reheated after leaving the high-pressure turbine by passing them through a secondary-combustion chamber to raise their temperature before continuing their expansion in the low-pressure turbine unit. Staged compression with intercooling, or staged expansion with reheat, may be applied to the gas-turbine power-plant cycle separately



or in combination with each other but, for reasons that will later develop, should always be used in combination with regeneration, as described in the earlier part of this article. The flow arrangement, when both are introduced into the cycle, is diagrammed in Fig. 12:15; note that the regenerative heat exchange takes place between the gases as they are exhausted from the low-pressure turbine and the air as it leaves the final stage of compression.

Exclusive of the effect of regeneration, the changes introduced into the air-standard cycle are illustrated in Fig. 12:16. In this figure, the basic Brayton cycle is shown as 1-*c*-3-*f*. The effect of staged compression with intercooling is indicated by the line 1-*a*, representing the first stage of compression, the line *a*-*b*, showing the effect of intercooling, and the line *b*-2, the second stage of compression. As a result of staging the compression, the work area 2-*c*-*a*-*b* is saved and therefore, in effect, added to the net work of the cycle, which is now traced as 1-*a*-*b*-2-3-*f*. If the cycle is reversibly performed, without regeneration, it will be noted that this extra work is not a free dividend but must be paid

for in terms of the extra heat, represented by area 2-*c*-*h*-*g*, that must be supplied the working fluid per cycle. With regeneration, because of the lower temperature at point 2, this extra heat may be recovered from the exhaust of the turbine and the heat supplied *by the source* (from *fuel*, in the real plant) need not increase; a net gain in efficiency is the result.

Turning now to the effect of staged expansion, with reheat, it is observed that a secondary combustion can be carried out in the real plant because it has been necessary to keep the temperature of the gases, as they enter the turbine, below the metallurgical limit and thus well below the maximum temperature that could result from combustion; this has been accomplished by using, in the first stage of combustion, a large amount of air in excess of that necessary to provide oxygen for the combustion of the fuel. The exhaust from the high-pressure turbine thus contains considerable uncombined oxygen and can support further combustion. Referring again to Fig. 12:16, it is noted that an extra dividend of work is secured by staged expansion, with reheat, which is represented by the area *d*-*e*-4-*f*; this comes at the expense of the extra heat supplied from the source (the fuel), as represented by area *d*-*e*-*j*-*i*. Without regeneration, the efficiency of the cycle would be lowered, for the ratio of these areas is

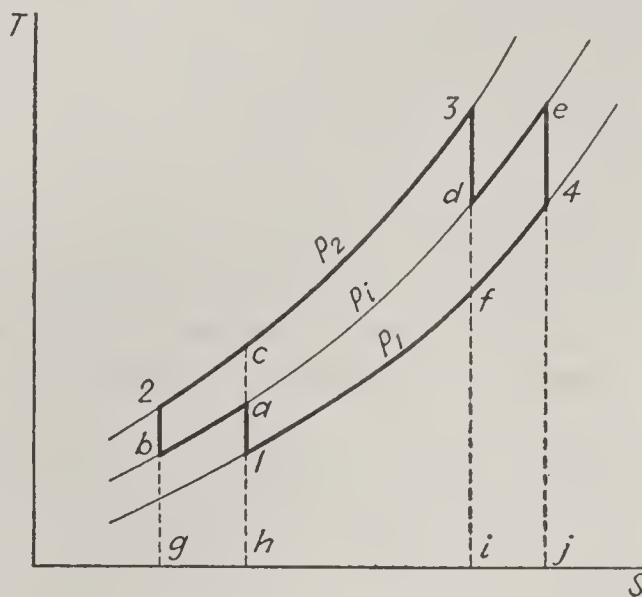


FIG. 12:16. The gas-turbine power-plant cycle—staged compression and expansion.

less than the efficiency of the basic Brayton cycle. But, with regeneration, the temperature of the exhaust gases is raised enough so that the exchange of heat due to regeneration is increased to the point where most of this extra heat need not come from the fuel but is saved by causing the air to enter the first stage of combustion at a higher temperature. In other words, a large part of the fuel used in the secondary combustion is saved in the primary combustion process.

*Example 12-9B.* Staged compression, with intercooling, and staged expansion, with reheat, are used in a gas-turbine power plant that operates between the over-all pressure limits 14 to 140 psia and between extreme temperatures of 90 and 2000°F, as in Example 12:8B. Two stages of compression and two stages of expansion are employed, as in Fig. 12:16, and the intermediate pressure is such that the work of compression and the work of expansion are divided equally between stages. Intercooling reduces the temperature of the air to 90°F at entrance to the second stage of compression, and reheat between turbine stages is to 2000°F. Compressor and turbine efficiencies are 85 per cent for each stage. Calculate the effect on cycle efficiency (a) without regeneration and (b) with ideal regeneration.

*Solution.* For equal division of work between stages in both compression and expansion,  $p_i/p_1 = (\frac{140}{14})^{\frac{1}{2}} = 3.16$  and  $p_i = (3.16)(14) = 44.3$  psia. With reference to Fig. 12:16,  $T_1 = 550^\circ\text{R}$ ;  $T_a = (550)(3.16)^{0.286} = (550)(1.39) = 765^\circ\text{R}$ ;  $T_b = 550^\circ\text{R}$ ;  $T_2 = (550)(3.16)^{0.286} = 765^\circ\text{R}$ ;  $T_d = 2460(1/3.16)^{0.286} = 1770^\circ\text{R}$ ;  $T_e = 2460^\circ\text{R}$ ;  $T_4 = 2460(1/3.16)^{0.286} = 1770^\circ\text{R}$ .

(Ideal) compressor work is  $(2)(0.24)(550 - 765) = -103$  Btu/lb

(Ideal) turbine work is  $(2)(0.24)(2460 - 1770) = 331$  Btu/lb

Actual compressor work is  $-103/0.85 = -121$  Btu/lb

Actual turbine work is  $(0.85)(331) = 281$  Btu/lb

Net work  $= 160$  Btu/lb

The actual temperatures at exit from the first and second stages of the turbine are higher than  $T_d$  and  $T_4$  as calculated above. They may be computed from the relation

$$\frac{T_3 - T_{d'}}{T_3 - T_d} = \frac{2460 - T_{d'}}{2460 - 1770} = 0.85 \text{ or } T_{d'} = 1873^\circ\text{R}$$

$$\frac{T_e - T_{4'}}{T_e - T_4} = \frac{2460 - T_{4'}}{2460 - 1770} = 0.85 \text{ or } T_{4'} = 1873^\circ\text{R}$$

Similarly, the temperature of the air at exit from the second stage of compression is designated as  $T_{2'}$ , where

$$\frac{T_b - T_2}{T_b - T_{2'}} = \frac{550 - 765}{550 - T_{2'}} = 0.85 \text{ or } T_{2'} = 803^\circ\text{R} = T_{a'}$$

(a) Without regeneration,

$$\begin{aligned} \text{Heat supplied in primary combustion} &= c_p(T_3 - T_{2'}) = 0.24(2460 - 803) \\ &= 396 \text{ Btu/lb} \end{aligned}$$

$$\begin{aligned} \text{Heat supplied in secondary combustion} &= c_p(T_e - T_{d'}) \\ &= 0.24(2460 - 1873) = 141 \text{ Btu/lb} \\ Q_s &= 537 \text{ Btu/lb} \end{aligned}$$

$$\eta = \frac{\text{net work}}{Q_s} = \frac{160}{537} = 0.298$$



Note that this is a lower cycle efficiency than was calculated in Ex. 12:8B.

(b) With ideal regeneration, the energy stored in the exhaust gas can be used to raise the temperature of the air as it enters primary combustion to  $T_4' (= 1873^\circ\text{R})$ . Then

$$\begin{aligned}\text{Heat supplied in primary combustion} &= c_p(T_3 - T_4') = 0.24(2460 - 1873) \\ &= 141 \text{ Btu/lb}\end{aligned}$$

$$\begin{aligned}\text{Heat supplied in secondary combustion} &= c_p(T_e - T_4') \\ &= 0.24(2460 - 1873) = 141 \text{ Btu/lb} \\ Q_s &= 282 \text{ Btu/lb}\end{aligned}$$

$$\eta = \frac{\text{net work}}{Q_s} = \frac{160}{282} = 0.567$$

This result, when compared with the efficiencies obtained in Example 12:8B and Example 12:9A, indicates that staged compression and expansion, *when used in combination with regeneration*, may have a beneficial effect on the efficiency of the cycle.

**12:10. Jet Propulsion.** The gas-turbine power plant has assumed increasing importance in the field of airplane propulsion. What had come to be regarded as the conventional method of propulsion consisted of an airscrew, or propeller, to which power was furnished by an internal-combustion engine of the reciprocating type. The efficiency of the propeller dropped off sharply as the speed of its tips approached the velocity of sound, about 750 mph in air at sea-level temperature, less at the higher altitudes. Because of the composition of the rotative velocities of the propeller segments with the forward (translational) velocity of the airplane, these tip speeds exceeded considerably the translational velocity, and the propeller-driven aircraft was limited in its efficient operation to speeds below 500 mph. By utilizing the gas-turbine power plant, it was possible to by-pass this "roadblock." In this application, the expansion in the turbine is halted at a point where the turbine can deliver just sufficient power to drive the compressor; the gases, as they leave the turbine, are at a pressure and temperature which is elevated above that corresponding to point 4 of Fig. 12:9. Because of their elevation of pressure and temperature, these gases may be ejected rearward through a nozzle-shaped opening at high velocity, and their consequent change of momentum results in a forward-acting reaction force (thrust) on the airplane. The propulsive efficiencies attained by this method of providing thrust increase with airplane speed, and the handicap of the propeller is thus avoided.

The airplane gas-turbine power plant may, of course, be adapted for propeller drive by continuing the expansion to atmospheric pressure. A variant is found in the possibility of changing the limit of expansion so that power may be delivered to the propeller at low airplane speeds, when propeller drive is more efficient, and providing that, at the higher speeds, jet propulsion may take over. When the expansion in the turbine is intermediate between these two extremes, the propeller and the jet may

operate concurrently to provide the thrust that pulls the airplane along its flight path.

At least in the present stage of its development, the gas-turbine power plant is considerably less efficient than the reciprocating-engine type of airplane power plant, and this means that a greater weight of fuel must be carried to accomplish the same task; this is a handicap of considerable importance in airplane design, where weight has great significance. However, a part of this extra weight is saved in the weight of the power plant itself; the gas-turbine power plant weighs much less per unit of rated power than does the reciprocating engine.

The gas-turbine power plant, as a jet-propulsion device, may be classified as of the *continuous-firing air-stream* type. An example of the *intermittent-firing* air-stream jet-propulsion engine is the V-1 bomb (the "buzz bomb") used by the Germans in the Second World War. This is shaped in the form of a nozzle and is given a considerable initial velocity by being projected into the air by a launching mechanism with the axis of the nozzle along the line of flight. Fuel is injected into the air-stream ahead of the throat of the nozzle, and the resulting mixture is exploded by means of an electric spark. The backflow of the exploded charge is prevented by shutters, which are located at the forward end of the duct and which close at once when backflow starts. The exploded charge then expands to the rear through the throat and, owing to its increased momentum, provides the forward thrust that is necessary to maintain the speed of the bomb. When the exploded charge has been dissipated, the ram action of the air stream again opens the shutters and the cycle is repeated.

When the nozzle is projected through the air at velocities in excess of the velocity of sound, the shutters of the buzz bomb are no longer necessary; if the flow at the throat of the nozzle is supersonic, it has been shown in Chap. 11 that backflow cannot take place. This type of device is called an athodyd (from *aero-thermodynamic-duct*); like the gas-turbine jet engine, the athodyd is a continuous-firing device.

In both buzz bomb and athodyd the supply of heat from the source (the fuel) begins at a temperature not far from that of the atmosphere. The average temperature at which heat is supplied is thus lower, and the attainment of high efficiency in the utilization of fuel is handicapped in comparison with the gas turbine.

The rocket is a jet-propulsion device which carries not only fuel but also oxygen for its combustion. These reactants combine progressively, and the products of combustion are ejected rearward at high velocity. The weight of oxygen carried is a large part of the total weight of the rocket, and the performance of this type of jet-propulsion device is correspondingly handicapped in comparison with the air-stream type described above; however, it is not dependent on oxygen from the surroundings and



thus may operate outside the earth's atmosphere. The charge of reactants in the head of the rocket may be in the form of solids, as in the Fourth-of-July skyrocket, or may be liquids, as in the V-2 bomb. In either case, provision must be made for progressive, rather than instantaneous, combustion of the charge.

**12:11. The Holzwarth Cycle and the Explosion Gas Turbine.** The same reasoning that was used in extending the expansion process of the diesel cycle to form the Brayton cycle may be applied to the Otto cycle. The result is known as the Holzwarth cycle and is illustrated in Fig. 12:17. This cycle differs from the Brayton cycle in the substitution of constant-volume, in place of constant-pressure, combustion. Some attempts have

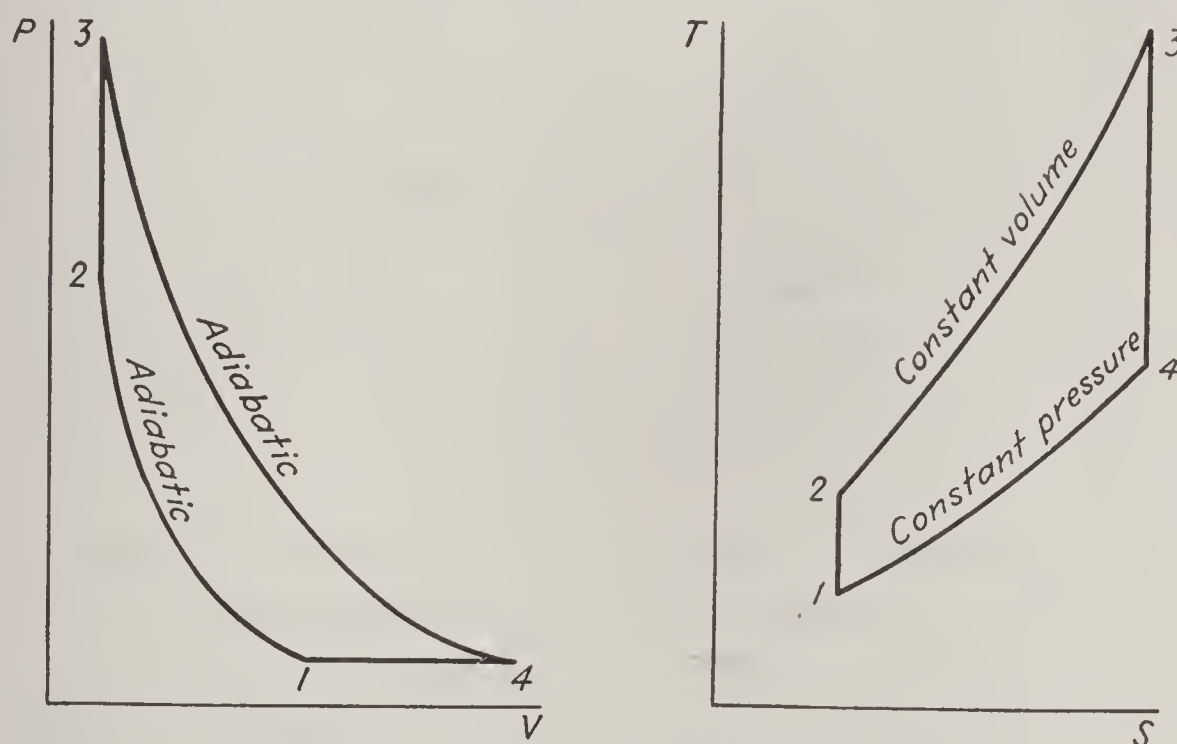


FIG. 12:17. Holzwarth air-standard cycle.

been made to utilize this cycle as the basis of a real power plant, and these have, in general, taken the form of an explosion gas turbine. This device includes a combustion chamber into which a charge of air is forced through the intake valve. Fuel is sprayed into this air charge through a fuel nozzle, and, with all valves closed, a spark ignites the mixture, exploding it. The exhaust valve then opens and permits the hot products of combustion to flow through nozzles and act on the blades of a turbine wheel, until the flow stops owing to a decrease of pressure. The action is intermittent, the gases impinging on the turbine buckets at variable velocity. This is not, as we have seen in Chap. 11, a condition that conduces to high turbine efficiency.

**12:12. External Combustion and the Closed Cycle.** Internal combustion is, of course, out of the question if the working fluid of the real engine is to follow the closed, controlled cycle of the heat engine. The classic example of the closed-cycle heat engine, using a gas as the working fluid, is the Carnot. The Carnot engine is purely an idealization for reasons

that have been fully covered in preceding pages. Three of the principal reasons will bear restatement at this time:

1. Heat is supplied to and rejected from the Carnot engine at constant temperature. This is not a practical method of heat exchange for a gas.

2. The net work of the Carnot engine is extremely small in comparison with the work of expansion and of compression; in other words, the mean effective pressure of the cycle is very low.

3. The working cylinder of the Carnot engine must perform both the function of a prime mover and of a heat exchanger, an impractical combination of duties in the real engine.

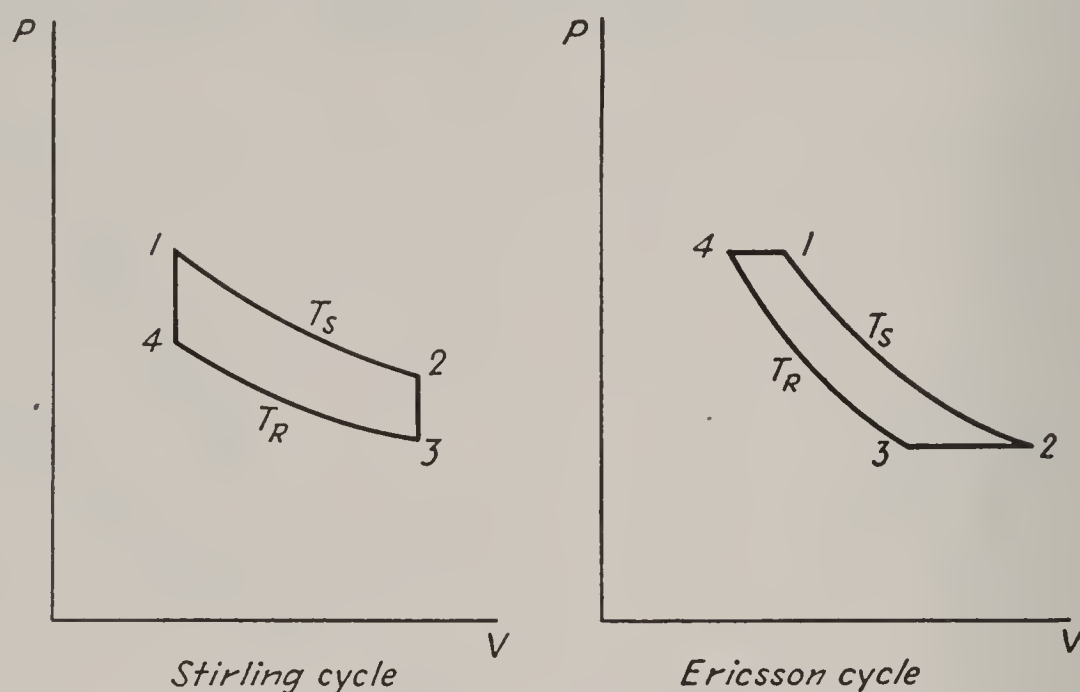


FIG. 12:18. Idealized cycles of the air engines.

These reasons are entirely sufficient to rule out the use of a real Carnot engine which uses a gas as the working fluid. They do not alter the value of the Carnot engine as a speculative device, an imaginary type of heat engine with which the ultimate in efficiency is associated. Let us, however, pass on to the cycles of real engines which can pass the gas system through a closed chain of processes, these engines thus being complete heat engines.

*The Regenerative Cycles.* The *Stirling* and the *Ericsson* cycles are shown in Fig. 12:18. These are the idealized forms of the cycles that are the basis of operation for the *Stirling* and the *Ericsson air engines*. Both cycles receive heat from the source only during the isothermal process 1-2 and reject heat to the refrigerator only during the isothermal 3-4. Each cycle rejects heat temporarily during the processes which are designated by the paths 2-3 of Fig. 12:18, but this heat is rejected to a regenerator which replaces it in the working fluid during process 4-1. Constant-volume regeneration, as described in Art. 4:6, is used in the *Stirling* cycle, regeneration at constant pressure in the *Ericsson* cycle. Both cycles may be shown to have an efficiency equal to  $(T_S - T_R)/T_S$  and thus to the



limiting standard set by the Carnot cycle; this has already been demonstrated for the Stirling cycle (see Chap. 4).

The real Stirling and the real Ericsson engines both include a working and a displacer cylinder and piston. To illustrate why these engines fall far short of the performance predicted by a thermodynamic analysis of their idealized cycles, the scheme of operation of the Stirling engine will be described below.

The displacer cylinder of the Stirling engine is closed at top and bottom, the source of heat (usually an open flame) being in contact with the bottom head and the refrigerator (either the open atmosphere or cooling coils) with the upper head. The displacer piston, as it moves vertically through its stroke, neither performs nor receives work but merely displaces the air from the bottom of the cylinder to the top, or vice versa, through side passages. These passages contain metal surfaces which exchange heat with the air and thus are capable of acting as regenerators. A passage leads from the displacer cylinder into the adjacent working cylinder, entering that cylinder beneath the working piston, and between that piston and the closed end of the working cylinder. At point 1 (Fig. 12:18) of the Stirling cycle, the displacer piston is at the upper end of its stroke and the working piston at the bottom of its cylinder. The volume of the enclosed air system is that of the displacer cylinder and regenerator passages, less the volume of the displacer piston. The air is at temperature  $T_s$  and is in contact with the lower head of the displacer cylinder; it therefore receives heat from the source through that head. This heat causes an expansion of the air, and the excess volume passes to the working cylinder and does work on the working piston as it moves through its upward stroke; by proper adjustment of the rate of movement of the working piston to the rate of heat supply, this expansion may be conceived as taking place at constant temperature. When the working piston reaches the top of its stroke, process 1-2 has been completed and the system has a volume  $V_2$ , greater by the displacement of the working piston than  $V_1$ , but still is at the temperature  $T_s$ ; thus  $p_2 < p_1$ . When point 2 is reached, the displacer piston, which has remained stationary at the top of its cylinder during the power stroke 1-2 of the working piston, begins to move downward; the working piston is now stationary. As it falls, the movement of the displacer piston produces no change in the total volume of the air system; the air is merely displaced from the bottom to the top of that piston, passing through the regenerator in transit. The material of the regenerator is cool and absorbs heat from the air so that this air issues into the space atop the displacer piston at the lower temperature  $T_R$ . When the downward stroke of the displacer piston has been completed, the air of the system has the volume  $V_3$  (equal to  $V_2$ ) and, because the temperature has been decreased, the lower pressure  $p_1$ .

The air is now in contact, through the upper head of the displacer cylinder, with the refrigerator, and heat begins to flow from the enclosed system to the refrigerator. This is the beginning of process 3-4, which continues with the displacer piston stationary at the bottom of its cylinder and the working piston falling at a rate such that the temperature of the air remains constant at  $T_R$ . When the working piston has reached the end of its return stroke, the volume is again the same as at point 1, but, because the temperature is  $T_R$ , the pressure  $p_4 < p_1$ . The only step necessary to return to point 1 at which we started the cycle is for the displacer piston to return to the top of its cylinder, with the working piston stationary at the bottom of its travel. This returns the air through the regenerator, which is hot because of the heat it received during process 2-3, and the air system issues into the space below the displacer piston (and in contact with the source through the lower head of the displacer cylinder) at the temperature  $T_s$ . Note that, in causing this temperature rise in the air, the regenerator has been cooled and is in a condition to perform its function of cooling the air during process 2-3, as the cycle is retraversed.

In the foregoing description, the operation of the Stirling engine has been highly idealized. The real engine obtains an approximation of alternate movement of displacer and working pistons by connecting them to the engine shaft through a  $90^\circ$  bell-crank arrangement, the displacer-piston crank being  $90^\circ$  ahead of the working-piston crank; this means that each piston, in turn, is not absolutely stationary while the other carries out its stroke. We have already observed that the isothermal process, not being subject to close control, is not a practical method of transferring heat to or from a gas system. There are large inherent irreversibilities connected with the practical application of the process of regeneration. The use of the displacer cylinder as a heat exchanger limits the performance of the engine by limiting the rate of heat transfer, and so the capacity of the air engine; engines of this type are exceedingly large in comparison with the power they may develop, and this factor has the effect of increasing the relative magnitude of losses due to mechanical friction. The effect of these considerations is to cause the efficiency of the real air engine to be only a small fraction of that predicted from an analysis of its idealized cycle. Air engines are not of present-day importance as prime movers, but they do exemplify a type of real engine, using a gas as the working fluid, that is a heat engine in principle. Being simple, and largely foolproof, in operation, they still are used in small sizes.

*The Closed-cycle Gas-turbine Power Plant.* External combustion may be applied to the gas-turbine power plant, as shown in the flow diagram of Fig. 12:19, and, combined with a cooling of the exhaust gases to atmospheric temperature, as also shown in that figure, can close the cycle and



convert the plant to a complete heat engine. If the heat-rejection process is omitted, the cycle is said to be semiclosed.

The advantages which can be seen in the application of the closed cycle to the gas-turbine power plant include:

1. The use of a cheaper fuel, such as coal, is possible.
2. A clean working fluid passes through both compressor and turbine, thus reducing damage to blading due to erosion and corrosion.
3. Higher pressures may be used at entrance to the compressor and around the cycle, making possible a reduction in plant size for a given power.

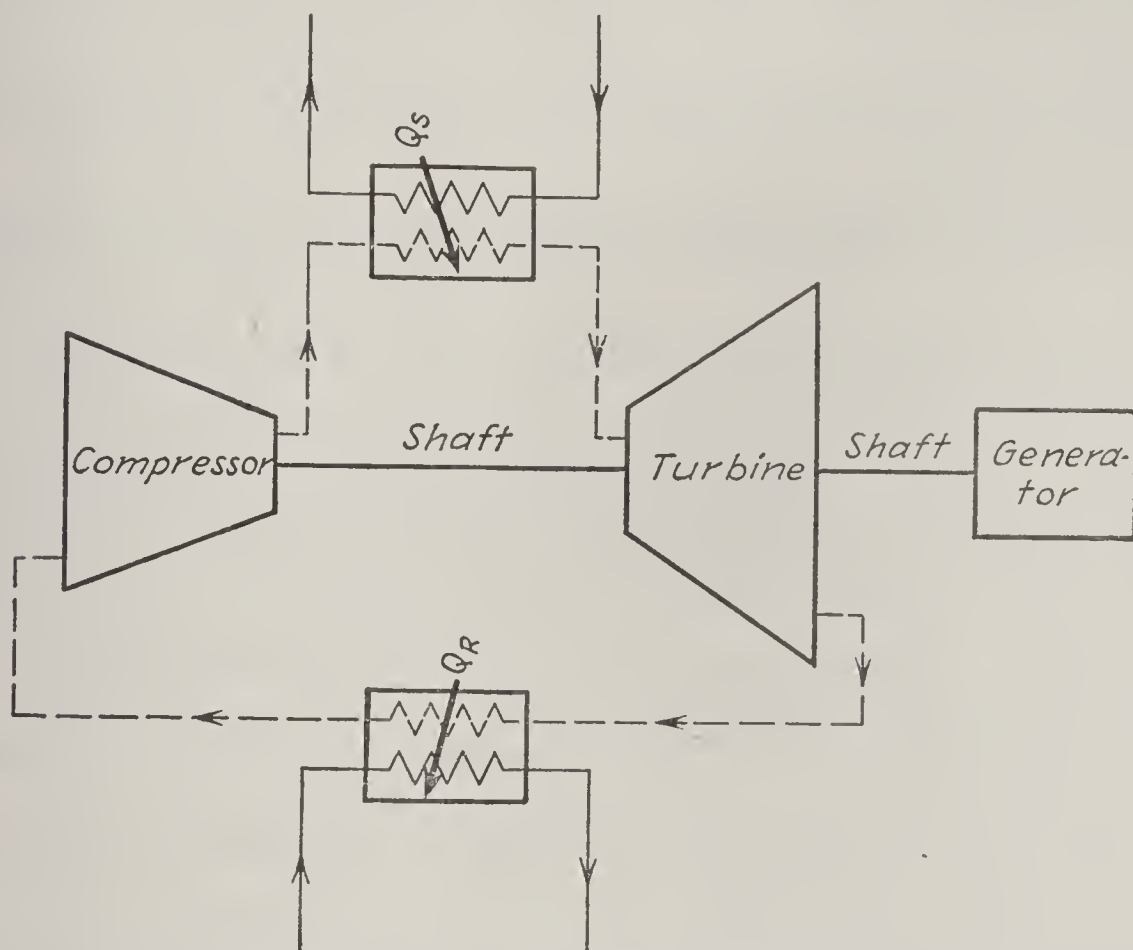


FIG. 12:19. The closed-system gas-turbine power-plant cycle.

4. An inert gas may be substituted for air, further lessening the likelihood of corrosion.

5. Fractional loads may be handled at high efficiency by varying the density of the gas system; this can be accomplished by providing for addition or subtraction of gas as the load demands.

The disadvantages may be listed as:

1. Additional complexity and consequent higher cost are incurred.
2. The introduction of a heat exchanger to replace the more efficient internal-combustion process is necessary.
3. A coolant is required.
4. The metallurgical limit imposes a lower maximum cycle temperature, because of the substitution of a heat exchanger for the combustion chamber.

## Problems

1. A test of an airplane engine which operates on the Otto cycle with a compression ratio of 8 shows it to be capable of delivering a horsepower-hour for an expenditure of 0.5 lb of gasoline (heat value = 18,500 Btu/lb). What percentage of air-standard efficiency is realized?
2. Work Example 12:3, changing the limiting temperatures of the cycle to 70 and 2500°F, respectively, but leaving other data unchanged. Compare your answers with those of the example, and comment on the effect of the change in data.
3. At the beginning of compression in an air-standard Otto cycle,  $V_1 = 1 \text{ ft}^3$ ,  $t_1 = 100^\circ\text{F}$ ,  $p_1 = 15 \text{ psia}$ . The temperature at the end of compression is 650°F, and the pressure  $p_3$  is 300 psia. Calculate the heat supplied, heat rejected, net work, air-standard efficiency, mean effective pressure, clearance, and compression ratio for this cycle.
4. The efficiency of an air-standard Otto cycle is 54 per cent. What is its clearance?
5. Plot the efficiency of the air-standard Otto cycle vs. its compression ratio for ratios between 4 and 12.
6. The pressure at the beginning of the compression stroke in an air-standard Otto cycle is 14 psia. At the end of the stroke it is 130 psia. What is the efficiency of the cycle?
7. Using the  $T$ 's diagram as a tool, show the effect of compression ratio on the efficiency of the air-standard Otto cycle.
8. To what cutoff percentage is a load ratio of 2 equivalent in a diesel engine with a compression ratio of 15? A compression ratio of 12? A compression ratio of 18?
9. At the beginning of compression in an air-standard diesel cycle,  $p_1 = 15 \text{ psia}$ ,  $t_1 = 100^\circ\text{F}$ , and  $V_1 = 1 \text{ ft}^3$ . The pressure at the end of compression is 600 psia. The temperature  $t_3 = 3000^\circ\text{F}$ . Calculate the heat supplied, the heat rejected, net work, air-standard efficiency, mean effective pressure, clearance per cent, cutoff per cent, and load ratio for this cycle.
10. Calculate the air-standard efficiency of a diesel cycle having a load ratio of 2 and a compression ratio of 14.
11. Calculate the air-standard efficiency of a diesel cycle having a cutoff percentage of 5 and a compression ratio of 15.
12. Based upon a load ratio of 2, plot the efficiency of the air-standard diesel cycle vs. its compression ratio for ratios between 8 and 18. Compare with the similar plot for the Otto air-standard cycle (see Prob. 5), and state your conclusions.
13. A diesel cycle has an air-standard efficiency of 0.60 when the load ratio is 1.8. What is its compression ratio?
14. Derive an expression for the efficiency of the air-standard dual cycle in terms of the absolute temperatures at points 1, 2, 3, 4, and 5. Based upon this expression, discuss the factors that affect the air-standard efficiency of this cycle.
15. For an air-standard dual cycle,  $p_1 = 14 \text{ psia}$ ,  $t_1 = 90^\circ\text{F}$ ,  $V_1 = 2 \text{ ft}^3$ ,  $V_2 = 0.15 \text{ ft}^3$ . Twenty Btu of heat is received by the charge at constant volume and 30 Btu at constant pressure. What are the pressure, temperature, and volume of the charge at the end of the adiabatic expansion? Calculate the heat rejected, net work, air-standard efficiency, compression ratio, clearance per cent, cutoff per cent, and mean effective pressure for this cycle.
16. Compare the Otto, diesel, and dual air-standard cycles on  $T$ 's coordinates on the basis of equal compression ratios. State your conclusions. Would you consider this a fair and reasonable basis of comparison?
17. Derive an expression for the efficiency of an air-standard Lenoir cycle in terms of the absolute temperatures at points 2, 3, and 4. Apply this expression to the calcula-



tion of the efficiency of a Lenoir air-standard cycle for which  $t_2 = 90^\circ\text{F}$  and  $t_3 = 3000^\circ\text{F}$ . Compare with the efficiencies calculated in Examples 12:3, 12:4, and 12:5 for Otto, diesel, and dual air-standard cycles operating between the same temperature extremes, and state your conclusions. Use the  $T$ 's diagram to make the same comparison.

18. Work Example 12:8A with the upper pressure of the cycle changed to 200 psia, all other data the same. Compare with the results obtained in the solution of the example, and discuss.

19. Assuming turbine and compressor efficiencies to be equal, how low could they fall under the conditions of Example 12:8A before the net output of the plant would vanish?

20. Work Example 12:8B with the upper pressure of the cycle changed to 200 psia, all other data the same. Compare with the results of the example and discuss.

21. Assuming turbine and compressor efficiencies to be equal, how low could they be under the conditions of Example 12:8B before the net output of the plant would become zero?

22. In Example 12:8A, how low could the highest temperature of the cycle drop before the net output of the plant would vanish when the compressor and turbine efficiencies were both 0.85?

23. Work Example 12:8B, part *d*, but change the compressor and turbine efficiencies to 0.80. Compare with the answer obtained in the solution of the example, and discuss.

24. Apply ideal regeneration to the cycle of Prob. 20, part *d*. Compare the cycle efficiencies with and without regeneration and discuss.

25. Apply ideal regeneration to the cycle of Example 12:8B, part *d*, but with compressor and turbine efficiencies of 0.80 (see Prob. 23). Calculate the efficiency of the cycle, and compare with the answers obtained in Example 12:9A and Prob. 23, discussing the effect of the change.

26. Work Example 12:9B, but change the upper pressure of the cycle to 200 psia.

27. Develop an expression for the efficiency of the explosion-gas-turbine air-standard cycle in terms of the temperatures at points 1, 2, 3, and 4. Using the  $T$ 's diagram, compare this cycle with the Otto cycle of the same compression ratio with respect to their efficiencies. According to this diagram, what factor causes the Otto cycle efficiency to be exceeded? Is the efficiency of the explosion-turbine cycle solely a function of its compression ratio? Discuss the effect of changing the pressure and temperature rise during explosion on the air-standard efficiency of the cycle.

28. For an explosion-turbine cycle, air-standard,  $p_1 = 14$  psia,  $t_1 = 110^\circ\text{F}$ .  $V_1 = 2$  ft<sup>3</sup>,  $p_3 = 300$  psia, and the compression ratio  $V_1/V_2$  is 5. Calculate the heat supplied, heat rejected, net work, and efficiency, for this cycle. What is the efficiency of the equivalent air-standard Otto cycle?

29. Show that the efficiency of the Ericsson cycle, with regeneration, will equal that of a Carnot cycle that operates between the same extremes of temperature.

### Symbols

$c$	a constant
$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$h$	specific enthalpy
$J$	proportionality factor
$k$	ratio of the specific heats, $c_p/c_v$
mep	mean effective pressure
$M$	mass flow rate, per cycle or per unit time

$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow, per cycle or per unit time
$R$	gas constant
$s$	specific entropy
$S$	entropy of a system
$T$	absolute temperature
$v$	specific volume
$V$	volume of a system
$W$	rate of work delivery, per cycle or per unit time

*Greek Letters*

$\eta$	efficiency
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*Subscripts*

$D$	displacement
$p$	constant pressure
$R$	refrigerator
$S$	source
$v$	constant volume



## CHAPTER 13

### THE RECIPROCATING STEAM ENGINE

**13:1.** The reciprocating engine of the steam power plant is, like the turbine, not a heat engine since steam enters and leaves across its boundaries. It may take the place of the turbine in the plant and so form a part of the steady-flow heat engine described in Art. 3:8. It differs from the turbine, among other respects, in that the flow of steam is not steady and continuous, as in the turbine, but intermittent in character. However, the reciprocating engine follows a machine cycle, and the over-all effect of its operation may be studied by applying the energy equation of steady flow, as suggested in Art. 3:9.

Some of the basic features of the reciprocating steam engine are illustrated in Fig. 13:1. Steam is admitted to a cylinder in which it operates to impart reciprocating motion to a piston; this reciprocating motion is converted into rotary motion through the action of a piston rod, crosshead, connecting rod, and crank. Referring to the illustration, the steam chest receives steam directly from the steam generator (the boiler, or boiler-superheater, unit of the steam-power-plant heat engine) and therefore contains

steam at full boiler pressure while the engine is in operation. The inlet valves operate alternately to admit and to shut off the flow of live steam to the two sides of the piston; the exhaust valves alternately open and release the charge, so that it may flow into the exhaust line and thence to the condenser, and close, bringing to an end the escape of expanded steam from the cylinder. The cylinder, as is common in steam-engine design, is double-acting, *i.e.*, as steam is admitted and expanded on one side of the piston, it is exhausted from the other end of the cylinder; thus a separate cycle of operation is carried out on each side of the piston, approximately doubling the capacity of a cylinder of given size. Double action is possible since the steam temperature is not high enough to cause

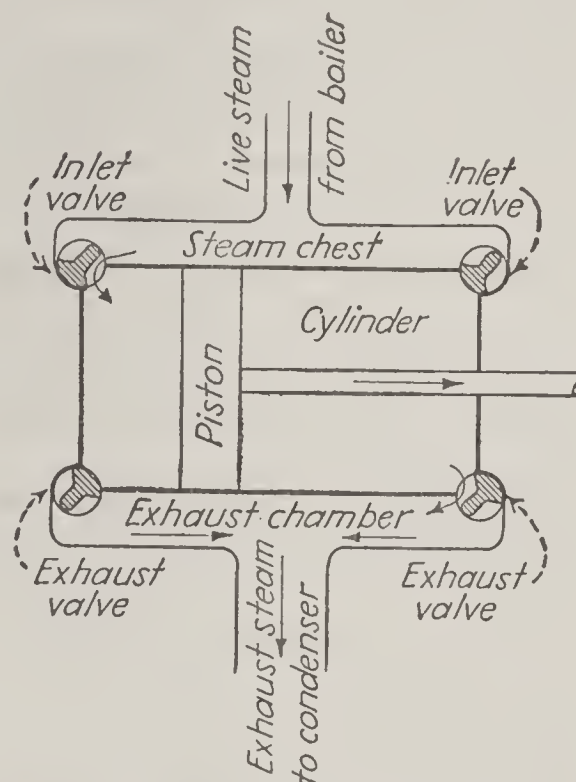


FIG. 13:1. The reciprocating steam engine.

cooling of the cylinder and piston to be a problem; deliberate cooling of cylinder surfaces, as in the internal-combustion engine, is not necessary, and the real steam engine is more nearly an adiabatic device than is the real internal-combustion engine.

Considering individually the two cycles of operation that are carried out in the cylinder of a double-acting engine, the admission of live steam usually takes place through only a part of the power stroke; after the supply has been cut off by the closing of the inlet, or *steam*, valve, the charge continues to expand until the piston reaches the end of its stroke. It is *fully* expanded only if the pressure has dropped to exhaust (condenser) pressure before the exhaust valve opens. Expansion in the real engine is seldom carried to this point since, as will be explained later, the losses outweigh the gains; thus, when the exhaust valve opens near the end of the power stroke, a rapid drop in pressure takes place as the partly expanded charge begins to escape into the exhaust passage. The exhaust valve remains open during the major portion of the return stroke of the piston; after it closes, the portion of the charge that remains in the cylinder is compressed into the clearance space. As, or shortly before, the piston reaches its limit of motion on the return stroke (its dead-center position), the intake valve opens, a fresh charge of live steam begins to enter, and the cycle is retraced. The valves are opened and closed mechanically, being driven by a mechanism that operates off the engine shaft. The action of the valves is described in terms of the *events* which they control. The opening of the intake valve is called *admission*, and its location in the cycle is described in terms of the percentage of piston stroke yet to be covered before the dead-center position at the beginning of the power stroke is reached. *Cutoff* marks the closing of the inlet valve, its location being stated in terms of the percentage of the power stroke that has been traversed at the time the valve closes. *Release* is the name applied to the opening of the exhaust valve, and the position of the event is described on the same basis that is used for cutoff. Finally, the closing of the exhaust valve is termed *compression*, located as occurring at a percentage of stroke determined in the same manner as for admission. Thus, in the location of all events of the cycle, the dead-center position of the piston at the beginning of its power stroke is conventionally used as the reference position.

In the elementary form of the steam engine, the events are located at fixed and constant percentages of the stroke as long as the engine is in operation; in order to change their position, the engine must be shut down and the valve-operating mechanism adjusted. In more advanced design, the percentages at which the events occur may be controlled, either manually or automatically, while the engine is running.

The type of engine cylinder illustrated in Fig. 13:1 is only one of the



many forms in which the steam engine is designed and built. For example, here the inlet and exhaust valves are distinct and separate, each having a semirotary motion of its own, and the location of inlet and exhaust events may be controlled independently of each other; in a type which is more common in practice (called the slide-valve engine), a single valve controls all events on both ends of the cylinder, and the exhaust steam leaves through the same openings (called *ports*) as are used by the live steam as it enters. The inlet ports always lead to the ends of the cylinder, but when a separate exhaust valve is used, it may be placed at a considerable distance from the cylinder head, as in the *uniflow* engine to be later described.

**13:2. The Reversible Adiabatic Engine.** The indicator diagram of a reversible adiabatic engine, without clearance, is illustrated in Fig. 13:2.

The intake valve opens at point 3, the pressure mounts to the supply pressure while the piston is still stationary at the end of its stroke (3-4), and line 4-1 represents the induction of the charge as the piston begins its power stroke, point 1 being the point of cutoff. During this portion of the power stroke, the work performed on the piston is represented by the area 4-1-a-0; if the weight of the charge is designated as  $M$ , this area is  $MP_1v_1$ . After cutoff, and until release at point 2, the charge expands

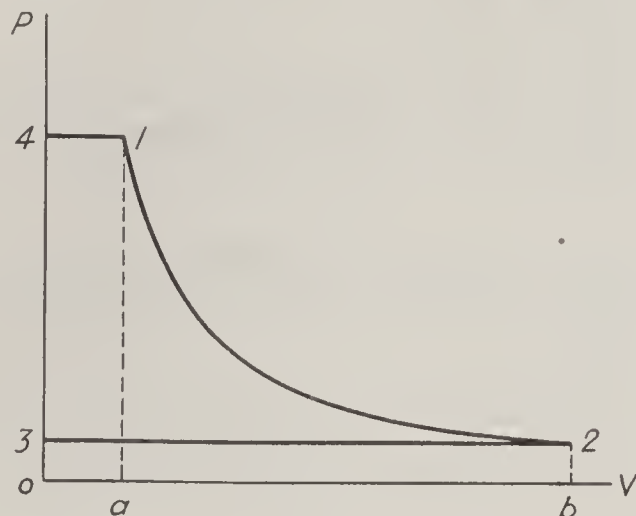


FIG. 13:2. Indicator diagram of reversible adiabatic engine without clearance.

isentropically, doing work on the piston equal to the area 1-2-b-a; since this expansion is adiabatic, an application of Eq. (2:3) shows that this work area equals  $JM(u_1 - u_2)$ . Finally, the exhaust valve remains open during the return stroke, closing simultaneously with the opening of the intake valve (at point 3), and the work done *by* the piston (negative work) during this stroke is equal to the area 2-3-0-b; this area is  $-MP_2v_2$ . Summing up the work areas, the net work of the cycle is  $MP_1v_1 + JM(u_1 - u_2) - MP_2v_2 = JM(h_1 - h_2)$ . Since points 1 and 2 lie on a line of constant entropy, we may designate the work of the reversible cycle as

$$W_{\text{rev cycle}} = JM(h_1 - h_2)_s$$

This cycle, as a reversible cycle, delivers the maximum possible amount of work under the given conditions, and the ideal net work for the adiabatic-engine cycle is therefore, in Btu per pound of steam flowing through the engine,  $(h_1 - h_2)_s$ , where the subscript 1 refers to the condition of the steam as it is supplied the engine and the subscript 2 to a state having the

same entropy but a pressure equal to condenser (exhaust) pressure. It is noted that the reversible adiabatic engine fully expands the charge of steam; if the state of the steam as it is supplied the reversible engine and the exhaust pressure are both constant, the cutoff is fixed at a definite percentage of the stroke of the reversible adiabatic engine.

The introduction of clearance, necessary in the real engine to cushion the piston as it changes the direction of its motion, does not mean that a

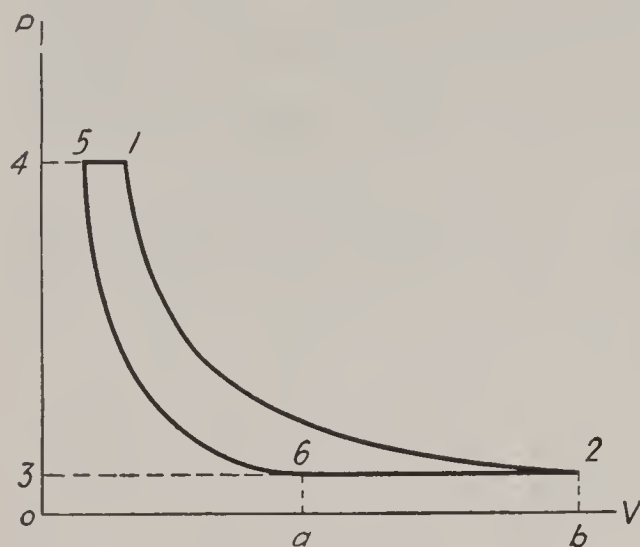


FIG. 13:3. Indicator diagram of reversible adiabatic engine, with clearance.

reversible adiabatic engine is no longer conceivable or that the ideal amount of work that may be performed per pound of steam supplied the engine will be any different. In Fig. 13:3 the cycle of a reversible adiabatic engine, with clearance, is shown by the full lines, the dashed lines corresponding to the equivalent cycle, without clearance, as in Fig. 13:2. In this case the piston does not move into contact with the cylinder head but leaves the clearance volume  $V_5$  between it and the head as it

reaches the end of its stroke. The amount of clearance is expressed in per cent of piston displacement, or

$$\text{Clearance, per cent} = \frac{100V_5}{V_D} = \frac{100V_5}{V_2 - V_5} \quad (13:1)$$

In the reversible adiabatic cycle of Fig. 13:3, the exhaust valve closes at point 6, trapping a portion of the charge having the volume  $V_6$  at the exhaust pressure. The weight of steam thus trapped is called the weight of *cushion steam* and will be designated as  $M_c$ . As the piston continues its return stroke, this cushion steam is compressed isentropically into the clearance space; when the piston reaches the end of its stroke, the steam has reached the supply pressure at point 5. At point 5, the inlet valve opens, and the fresh charge begins to flow into the cylinder; this fresh charge is called the *flow steam*, and its weight will be designated as  $M_f$ . The rest of the cycle is the same as for the reversible adiabatic engine, without clearance, when that engine contains, at cutoff, a charge having a weight equal to  $M_c + M_f$ . Note that the *condition* of the steam has not changed between points 5 and 1; only the weight is different. The same may be said with regard to points 6 and 2. Therefore we may write the relation

$$\frac{V_5}{V_1} = \frac{V_6}{V_2} = \frac{M_c}{M_c + M_f} \quad (13:2)$$



and observe that the position of compression (point 6) must, like the position of cutoff, be fixed and constant for the reversible adiabatic engine with a given clearance. The net work of the reversible cycle is represented by area 5-1-2-6; this work is performed at the expense of supplying a weight  $M_f$  of fresh charge. The work area equals area 4-1-2-3 less area 4-5-6-3. Area 4-1-2-3 is the net-work area for the reversible cycle, without clearance, which receives a charge weighing  $M_c + M_f$  and therefore, as shown above, is equal to  $(M_c + M_f)(h_1 - h_2)_s$ , in Btu. Similarly, area 4-5-6-3 may be shown to be equal to  $M_c(h_5 - h_6)_s$  or, since the states at points 5 and 6 are, respectively, the same as at points 1 and 2, to  $M_c(h_1 - h_2)_s$ . Thus the net work of the reversible cycle with clearance is

$$\left(\frac{W}{J}\right)_{\text{rev cycle}} = (M_c + M_f)(h_1 - h_2)_s - M_c(h_1 - h_2)_s = M_f(h_1 - h_2)_s \quad (13:3)$$

A comparison of Eq. (13:3) with the equivalent expression for the reversible engine without clearance shows that the same net amount of work, *per pound of flow steam*, is performed with or without clearance.

**Example 13:2A.** Steam is supplied a double-acting reversible adiabatic engine, without clearance, at 130 psia dry and saturated. Exhaust pressure is 14.7 psia. The engine has a bore of 10 in., a 12-in. stroke, and operates at 180 rpm. Neglect the volume of the piston rod. (a) What is the percentage of cutoff? (b) What weight of flow steam is supplied per cycle? (c) What work is delivered per cycle? (d) What horsepower does the engine deliver?

*Solution:*

(a) The specific volume of the steam at cutoff (point 1, Fig. 13:2) is that of dry and saturated steam at 130 psia, or  $v_1 = 3.455$  ft<sup>3</sup>/lb. The specific enthalpy is  $h_1 = 1191.7$  Btu/lb, and  $s_1 = 1.5812$ . Following a line of constant entropy from point 1 to a pressure of 14.7 psia on the Mollier diagram, the properties of the steam at the end of expansion may be read as  $h_2 = 1033$  Btu/lb and  $x_2 = 0.878$ . Then  $v_2 = (0.878)(26.80) = 23.53$  ft<sup>3</sup>/lb. The percentage of cutoff is

$$\frac{V_1}{V_2} = \frac{v_1}{v_2} = \frac{3.455}{23.53} = 0.147, \text{ or } 14.7 \text{ per cent}$$

(b) The volume at cutoff is

$$V_1 = \frac{\pi}{4} \frac{(10)^2(12)(0.147)}{1728} = 0.08 \text{ ft}^3$$

The weight of flow steam per cycle is

$$M = \frac{V_1}{v_1} = \frac{0.08}{3.455} = 0.0232 \text{ lb per cycle}$$

(c) Net work per cycle =  $M(h_1 - h_2)_s = 0.0232(1191.7 - 1033)$   
 $= 3.68$  Btu, or 2860 ft-lb, per cycle

(d)  $\text{hp} = \frac{(2860)(2)(180)}{33,000} = 31.3 \text{ hp}$

**Example 13:2B.** The same as Example 13:2A, except that the reversible adiabatic engine has a clearance of 8 per cent at both ends of the cylinder. Calculate (a) percentage of cutoff, (b) percentage of compression, (c) weight of cushion steam per cycle, (d) weight of flow steam per cycle, (e) work delivered per cycle, and (f) horsepower delivered by the engine.

*Solution:*

(a) Reference is to Fig. 13:3. From Example 13:2A,

$$\frac{V_1}{V_2} = \frac{v_1}{v_2} = 0.147$$

From Eq. (13:1),

$$V_5 = 0.08(V_2 - V_5) \text{ or } \frac{V_2}{V_5} = \frac{1.08}{0.08} = 13.5$$

Then

$$\frac{V_1}{V_5} = \frac{V_1}{V_2} \frac{V_2}{V_5} = (0.147)(13.5) = 1.98$$

$$\text{Cutoff} = \frac{V_1 - V_5}{V_2 - V_5} = \frac{V_1/V_5 - 1}{V_2/V_5 - 1} = \frac{1.98 - 1}{13.5 - 1} = 0.079, \text{ or } 7.9 \text{ per cent}$$

$$(b) \frac{V_6}{V_5} = \frac{V_2}{V_1} = \frac{v_2}{v_1} = \frac{1}{0.147} = 6.8$$

$$\text{Compression} = \frac{V_6 - V_5}{V_2 - V_5} = \frac{V_6/V_5 - 1}{V_2/V_5 - 1} = \frac{6.8 - 1}{13.5 - 1} = 0.456, \text{ or } 45.6 \text{ per cent}$$

$$(c) \text{ Piston displacement} = \frac{\pi}{4} \frac{(10)^2(12)}{1728} = 0.547 \text{ ft}^3$$

$$V_6 = (0.456 + 0.08)(0.547) = 0.293 \text{ ft}^3$$

$$M_c = \frac{0.293}{26.80} = 0.0109 \text{ lb per cycle}$$

$$(d) V_1 = (0.079 + 0.08)(0.547) = 0.087 \text{ ft}^3$$

$$M_f + M_c = \frac{0.087}{3.455} = 0.0252 \text{ lb per cycle}$$

$$M_f = 0.0252 - 0.0109 = 0.0143 \text{ lb per cycle}$$

$$(e) \text{ Net work per cycle} = M_f(h_1 - h_2)_s = 0.0143(1191.7 - 1033) = 2.27 \text{ Btu, or } 1770 \text{ ft-lb per cycle}$$

$$(f) \text{ hp} = \frac{(1770)(2)(180)}{33,000} = 19.3 \text{ hp}$$

**13:3. The Real-engine Cycle.** An indicator diagram such as might be obtained during the operation of a real engine is shown by the full lines of Fig. 13:4. For purposes of comparison, the dashed lines show a reversible cycle having the same clearance volume  $V_5$  and the same volume at cutoff  $V_1$ . Admission ( $A$ ) occurs almost at dead center in this real-engine cycle, as in the cycle of the reversible engine, but at a pressure somewhat below the supply pressure. The cutoff is designated as  $CO$  and the lowering of line  $c-CO$  below the admission line of the reversible cycle is due to the differential of pressure necessary to force the steam through the intake



valve and passages. Because of the lowering of point  $CO$  below point 1, the expansion line between cutoff and release ( $R$ ) lies below the ideal expansion curve. The exhaust valve opens for release before the end of the stroke, and the stroke is much shorter than that of the reversible engine. This causes the toe-shaped work area of the reversible cycle between  $R$  and point 2 to be lost, but this area is relatively small and could be recovered only at the expense of a greatly lengthened stroke, with correspondingly increased losses due to engine friction. The irreversible throttling of the steam as it passes through the exhaust valve, when that valve is first opened, is shown as line  $R-d$  of the real-engine cycle. The exhaust line  $d-K$  is raised above the line 2-6 by the resistance to flow offered by the exhaust valve and passages, and compression (point  $K$ ) is

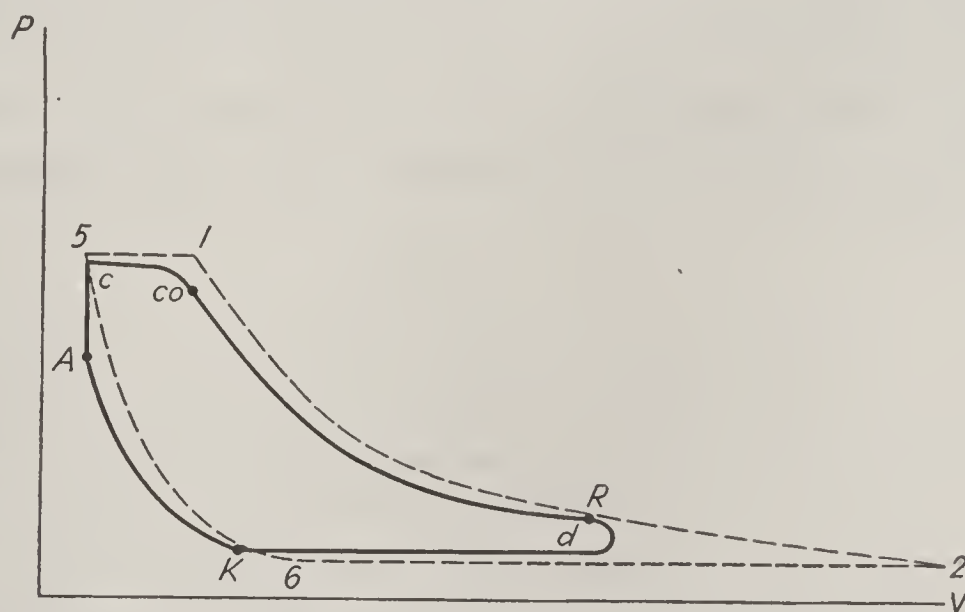


FIG. 13:4. Comparison of real- and reversible-engine diagrams.

delayed somewhat, resulting in the lower pressure at admission and lowering the compression curve for the cushion steam. The losses of work area due to the lowering of line  $c-CO$  below 5-1 and the raising of line  $d-K$  above 2-6 are called *wiredrawing* losses, and the loss of the toe-shaped area of the reversible cycle to the right of  $R$  is termed an *incomplete-expansion* loss.

A comparison of the areas of the two cycles of Fig. 13:4 does not show the real cycle to enclose a much smaller area than that enclosed by the reversible cycle, and the thought occurs that the losses due to the various irreversibilities are small. This would be true if the weight of flow steam were the same for each cycle; this is not the case for, owing to effects to be discussed later, the weight of flow steam which must be supplied per cycle to the real engine is considerably greater than that necessary for the reversible engine. The work measured by the only slightly smaller area of the real-engine cycle is therefore credited to a larger weight of steam, and the relative performance of the real engine is not as good as would appear from a comparison of the areas of Fig. 13:4 alone.

**13:4. Steady-flow Analysis of the Reciprocating Engine.** Equation (3:5) may be applied to the purpose of analyzing the condition of the

working fluid at exit from the real steam engine. The results of an economy test of the engine will show the amount of work performed on the piston (from the indicator diagram) per pound of steam supplied. Then

$$h_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} + {}_1Q_{2'} = h_{2'} + \frac{\bar{V}_{2'}^2}{2Jg} + \frac{z_{2'}}{J} + \frac{W_e}{J}$$

in which the subscript 1 refers to the condition of the steam at a section of the supply line ahead of the engine and subscript 2' to the state at a section of the exhaust line leaving the engine.  ${}_1Q_{2'}$  is the heat exchange with the atmosphere per pound of steam supplied and, being negligible, may be assigned a value of zero.  $W_e$  is obtained, as stated above, from the indicator card, the total indicated work of the engine during the period of the test being divided by the total weight of steam supplied during that period. The differences between the stored energy due to velocity and elevation at entrance and exit are negligible and may be dropped from the equation. Then

$$h_{2'} = h_1 - \frac{W_e}{J} \quad (13:4)$$

In the usual application of this equation,  $h_1$  and  $W_e$  are known from the data and results of a test, and  $h_{2'}$  is the dependent quantity; however, any two of the quantities of Eq. (13:4) will suffice to determine the third. Thus, if the equation is applied to the ideal reversible engine,  $h_2$  is the specific enthalpy corresponding to a state having a pressure equal to that at which steam is exhausted from the engine and the same entropy as the steam supplied the engine, and  $W_e = J(h_1 - h_2)_s$ .

**13:5. Engine Efficiency.** The term engine is applied in thermodynamics to prime movers, whether they be of the reciprocating or the turbine type. It must not be confused with heat engine, which, as we have seen, has an altogether different meaning in thermodynamics. The efficiency of a heat engine is a ratio of work performance to heat flow, but the efficiency of an engine, whether a reciprocating engine or a turbine, is the ratio of the work output of the real engine to that of an ideal (reversible adiabatic) engine to which the working fluid is supplied at the same rate and at the same state and which exhausts to the same pressure. In the absence of a refrigerator at absolute zero of temperature, it is impossible for even the ideal heat engine to have an efficiency of 1; on the other hand, the perfect prime mover does have that *engine efficiency*. We may write

$$\eta_e = \frac{W_e}{J(h_1 - h_2)_s} \quad (13:5)$$

where  $\eta_e$  is the engine efficiency, a decimal fraction,  $W_e$  is the work per-



formed by the real engine per pound of working fluid supplied to it, and  $(h_1 - h_2)_s$  is the drop in specific enthalpy between the state at which the fluid is supplied the real engine and a state having the same entropy but a pressure equal to that at which the working fluid is discharged from the engine. The difference  $(h_1 - h_2)_s$  is called the isentropic drop of enthalpy and may conveniently be designated as  $-\Delta h_s$ . The effect of the irreversibilities of the real engine is to decrease the work output below the standard set by the reversible adiabatic engine and so, from Eq. (13:4), to raise  $h_2$  above its value for the ideal engine; this higher value has been designated as  $h_{2'}$  in Eq. (13:4). The indicated work per pound of flow steam supplied the real engine is then  $h_1 - h_{2'}$ , or simply  $-\Delta h$ . In these terms, the engine efficiency of the real engine becomes

$$\eta_e = \frac{h_1 - h_{2'}}{(h_1 - h_2)_s} = \frac{\Delta h}{\Delta h_s} \quad (13:6)$$

Equation (13:6) is graphically explained in Fig. 13:5, a Mollier diagram, in which 1-2 is the process carried out in the ideal engine and 1-2' represents the change in state in the real engine. A comparison with Fig. 11:17 and with Eq. (11:27) will show that Eq. (13:6) is as valid for the turbine as for the reciprocating engine.

In other words, *turbine efficiency* is essentially the *engine efficiency* of a turbine type of engine.

The performance of various kinds of prime movers, both vapor and gas, is often compared in terms of their respective *thermal efficiencies*. The general definition of the thermal efficiency of an engine is the ratio of the work output to the heat supplied from the source during the same time period; thermal efficiency is thus equivalent to what has been called in these pages the efficiency of a heat engine. Unless the prime mover is a complete heat engine in itself, its thermal efficiency cannot always be calculated unless the action of other apparatus (such as the boiler of the steam power plant) through which the fluid passes is assumed. The thermal efficiency of a steam engine is thus really the efficiency of the heat engine of which it is a part. In the case of the internal-combustion engine, the denominator of the output/input ratio, which is the thermal efficiency, is the heat value of the fuel that is furnished the engine during the period of time required to deliver the work. Since the fuel is supplied directly to the prime mover, the use of the term thermal efficiency is more

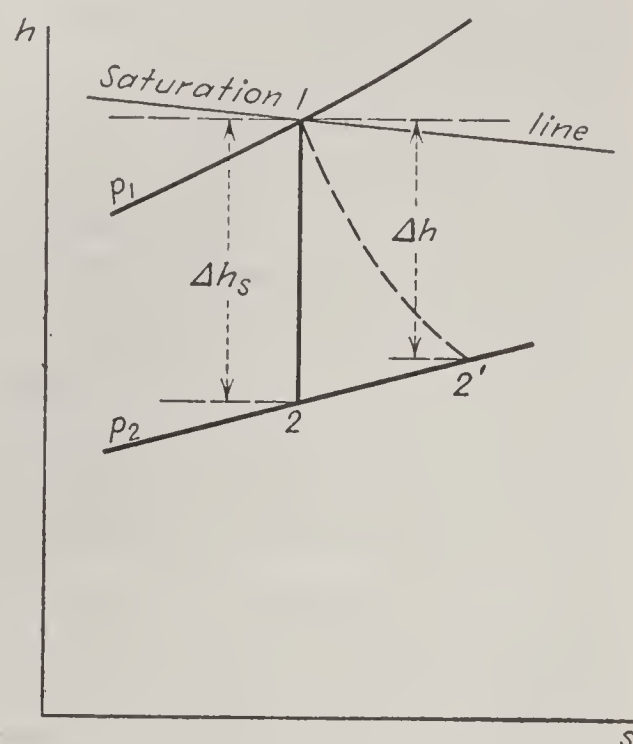


FIG. 13:5. Engine efficiency.

reasonable as applied to the internal-combustion engine, even though it is not a complete heat engine.

**13:6. Sources of Irreversibility in the Reciprocating Engine.** Some of the sources of irreversibility in the reciprocating engine have been suggested in Art. 13:3 and pictured in Fig. 13:4. These include the wire-drawing losses, due to pressure losses through the valves and valve passages and causing the loss of work area below line 5-1 and above line 2-6 in Fig. 13:4, and the incomplete-expansion loss, due to opening the exhaust valve before the fluid has dropped to exhaust pressure and causing the loss of the toe-shaped work area at the right-hand end of the ideal-engine diagram of that figure. The gain in work area because of the lowering of the compression line below that of the ideal diagram is more apparent than real since it comes at the expense of delayed compression and thus simply means that the weight of cushion steam is less for the real than for the ideal cycle. The work expended on the compression of this cushion steam is completely recovered by the ideal engine during the performance of its succeeding cycle of operation.

Figure 13:4 does not show nor does Art. 13:3 discuss what is undoubtedly the source of the most serious irreversibility, from the standpoint of its effect on the efficiency of the reciprocating engine. Although, in the course of its traversal of a complete cycle, the reciprocating engine is, very closely, an adiabatic device, there is a constant interchange of heat between the working fluid and the piston and the walls and head of the cylinder. During a part of the cycle this flow of heat is from the fluid into these surfaces and, during another part of the cycle, in the opposite direction. These flows of heat obviously arise from differences of temperature between the fluid and the engine parts with which it is in contact; the differences of temperature are the result of the intermittent character of the fluid flow through the engine.

The temperature of the fluid varies between extremes set by the temperature at which it is supplied and the lowest temperature that is reached in the course of its expansion in the engine. The fresh charge of flow steam, as it enters, comes in contact with metal surfaces which have been cooled by having been in contact with exhaust steam during at least a part of the return stroke of the piston. If the charge is supplied in the form of a saturated vapor, a part will be condensed in heating these surfaces and will not be available to contribute useful work during the expansion process; if supplied as a superheated vapor, the superheat will at least be reduced and some condensation is even likely to take place, with a similar effect on work output. This phenomenon is known as *initial condensation* and, in practice, often causes the quality at cutoff to be 0.80 or less, although dry steam was supplied the engine. The moisture in the steam occupies negligible volume, and a correspondingly greater weight



of vapor is required to fill the cutoff volume ( $V_1$  of Fig. 13:4) than for the reversible adiabatic engine; thus, for the real reciprocating steam engine, the weight of flow steam used per cycle is increased. Moreover, the moisture which has accumulated in the charge of the real engine at cutoff does not contribute toward the work performed during later expansion to release pressure to any appreciable degree.

As the expansion of the charge proceeds, after cutoff, the temperature of the vapor gradually decreases and soon drops below that of the surfaces with which it is in contact. The heat exchange is thereafter reversed in direction, and, during the latter part of expansion, after release, during exhaust and the early part of compression of the cushion steam, heat flows from the engine surfaces back into the fluid. This return of heat is called *reevaporation*; it has the effect of slightly lifting the lower part of the expansion curve, but the increase of useful-work area is minor and does not compare with the loss due to initial condensation. On the thermodynamic basis, the insignificance of work recovery because of reevaporation is partly explained by the lower temperature at which this heat return takes place; also, much of the heat is returned during the exhaust stroke, with no other effect than to raise the enthalpy of the fluid as it is discharged from the cylinder. The combined effect of initial condensation and reevaporation is an irreversibility of major magnitude and importance and is called the *cylinder condensation loss*.

**13:7. Hirn's analysis** is a method of evaluating the heat exchange between the fluid and the engine surfaces with which it comes in contact during the cycle of the reciprocating engine. To carry out the analysis, a typical indicator diagram is needed plus information as to the weight of flow steam received per cycle, its state as supplied the engine, the exhaust pressure, and the condition of the steam as it was exhausted from the engine. The engine bore, stroke, and clearance must also be known. The weight of flow steam is usually based on the result of an economy test at constant load over a suitable period of time; condenser data taken in the course of this test permit the calculation of the exit enthalpy of the steam.

In carrying out the Hirn analysis, the entire cycle is divided into four periods, and the heat exchange during each of these periods is separately determined. The four periods are:

1. Admission (starting with the event of admission and concluding at cutoff). During this period the fluid system within the cylinder is an open system, and Eq. (3:3) may be applied.

2. Expansion (beginning with cutoff and ending at release). The system is closed during this period, and Eq. (2:3) is applicable.

3. Exhaust (after release and until the event of compression). The system is again an open system during this period. Equation (3:3) is applied.

4. Compression (between the events of compression and admission). Again the system is a closed system, and Eq. (2:3) may be applied.

As it applies to the admission period, Eq. (3:3) may be written (neglecting energy quantities due to velocity and elevation as insignificant) in the form

$$(M_c + M_f)u_{co} - M_c u_A = - \frac{{}_A W_{co}}{J} + {}_A Q_{co} + M_f h_1$$

in which the subscripts *A* and *CO* refer to the events of admission and cutoff, respectively, and the subscript 1 to the state at which steam is supplied the engine;  $M_c$  and  $M_f$  are the weights of cushion and of flow steam per cycle, respectively;  ${}_A W_{co}$  is the work performed on the piston and may be obtained as the area between the line connecting admission and cutoff on the indicator diagram and the *V* axis of that diagram, expressed in foot-pounds; and  ${}_A Q_{co}$  is the heat exchange with the cylinder and piston during the admission period, a negative sign indicating heat flow from the charge of steam into the walls. The state of the fluid corresponding to any point on the cycle of the indicator diagram can be determined from the pressure and volume at that point, as measured from the indicator diagram, if the weight of fluid present in the cylinder is known. For example, at cutoff this weight is  $M_f + M_c$ ; of these two weight components,  $M_f$  is known from data secured before the Hirn analysis is applied.  $M_c$ , the weight of cushion steam, is conventionally calculated on the basis of the assumption that, at the point of compression (*K* of Fig. 13:4), the steam has a quality of 1; this is usually not far from the actual quality because of the effects of reevaporation and drainage of the condensate, but, in any event, the assumption does not lead to serious error because of the relatively small weight of cushion steam as compared with the flow steam. All terms of the equation may thus be separately determined except the heat flow during the admission period. Rearranging the equation into the form

$${}_A Q_{co} = (M_c + M_f)u_{co} - M_c u_A - M_f h_1 + \frac{{}_A W_{co}}{J} \quad (13:7)$$

this heat flow may be computed.

Applying Eq. (2:3) to the expansion period,

$${}_{co} Q_R = (M_c + M_f)(u_R - u_{co}) + \frac{{}_{co} W_R}{J} \quad (13:8)$$

in which the terms on the right-hand side of the equation are separately evaluated in a manner identical with that used in the case of the similar terms of Eq. (13:7).

Similarly, applying Eq. (3:3) to the exhaust period, we may write

$${}_R Q_K = M_c u_K + M_f h_2' - (M_c + M_f)u_R + \frac{{}_R W_K}{J} \quad (13:9)$$



in which  $h_2$  is the specific enthalpy of the exhaust steam and may be determined from test data taken from the condenser.

Finally, the application of Eq. (2:3) to the compression period gives

$${}_KQ_A = M_c(u_A - u_K) + \frac{{}_K W_A}{J} \quad (13:10)$$

The algebraic sum of the four individual heat flows should be found to be very nearly equal to zero. The difference from zero, if any, should be negative and represents heat transferred through the walls and head of the cylinder and into the surrounding atmosphere. In the absence of complete condenser data, it is sometimes necessary to fix the value of  $h_2$  by applying Eq. (13:4); this amounts to an assumption that the real engine is an adiabatic (though not a reversible) engine and assures that the sum of the four individual heat flows will be zero.

*Example 13:7.* A steam-engine economy test supplies the following data:

*Engine data:* Double-acting, 10-in. bore, 12-in. stroke, 180 rpm. Neglect piston-rod volume.

*Steam data:* Supply pressure, 130 psia, dry and saturated.

*Condenser data:* Exhaust pressure, 14.7 psia. Condensate temperature, 200°F. Weights, per hour: condensate, 1062 lb; cooling water, 31,800 lb. Temperatures, cooling water: inlet, 65°F; outlet, 96°F.

*Indicator-card data:* Scale of indicator spring, 80 psi/in. Length of indicator card, 4 in. Location of events: admission, 0 per cent, 90 psia; cutoff, 20 per cent, 115 psia; release, 95 per cent, 31 psia; compression, 30 per cent, 18 psia.

Indicator-card areas (measured to  $V$  axis at  $p = 0$  psia):

Admission period ( $A$ to $CO$ )	=	1.26 in. <sup>2</sup>
Expansion period ( $CO$ to $R$ )	=	2.24 in. <sup>2</sup>
Exhaust period ( $R$ to $K$ )	=	-0.54 in. <sup>2</sup>
Compression period ( $K$ to $A$ )	=	-0.66 in. <sup>2</sup>
Net (enclosed) area	=	2.30 in. <sup>2</sup>

Calculate (a) work per period per cycle and net work of the cycle, Btu; (b) indicated horsepower of the engine; (c) weights of cushion steam and flow steam per cycle; (d) quality at cutoff, release, and admission; (e) heat exchange with the walls during each of the four periods; (f) heat flow to the atmosphere per cycle; (g)  $h_2$  as for an adiabatic engine; (h) engine efficiency based on the indicated horsepower.

*Solution:*

(a) Piston displacement = 0.547 ft<sup>3</sup> (see Example 13:2B, part c). One square inch of indicator-card area =  $\frac{(80)(144)(0.547)}{(778)(4)} = 2.02$  Btu.

$$\frac{{}_A W_{CO}}{J} = 1.26(2.02) = 2.54 \text{ Btu}$$

$$\frac{{}_{CO} W_R}{J} = 2.24(2.02) = 4.52 \text{ Btu}$$

$$\frac{{}_R W_K}{J} = -0.54(2.02) = -1.09 \text{ Btu}$$

$$\frac{{}_K W_A}{J} = -0.66(2.02) = -1.33 \text{ Btu}$$

$$\text{Net work} = 4.65 \text{ Btu}$$

$$(b) \text{ ihp} = \frac{(4.65)(180)(2)(778)}{33,000} = 39.4 \text{ hp}$$

$$(c) V_A = (0.08)(0.547) = 0.0438 \text{ ft}^3$$

$$V_{CO} = (0.08 + 0.20)(0.547) = 0.1535 \text{ ft}^3$$

$$V_R = (0.08 + 0.95)(0.547) = 0.5630 \text{ ft}^3$$

$$V_K = (0.08 + 0.30)(0.547) = 0.2080 \text{ ft}^3$$

The quality at compression is assumed to be 1. Then

$$M_c = \frac{V_K}{v_g \text{ at } 18 \text{ psia}} = \frac{0.2080}{22.17} = 0.0094 \text{ lb}$$

$$M_f = \frac{1062}{(180)(2)(60)} = 0.0492 \text{ lb per cycle}$$

$$(d) x_{CO} = \frac{V_{CO}}{(M_c + M_f)(v_g \text{ at } 115 \text{ psia})} = \frac{0.1535}{(0.0094 + 0.0492)(3.882)} = 0.675$$

$$x_R = \frac{V_R}{(M_c + M_f)(v_g \text{ at } 31 \text{ psia})} = \frac{0.5630}{(0.0586)(13.33)} = 0.72$$

$$x_A = \frac{V_A}{M_c(v_g \text{ at } 90 \text{ psia})} = \frac{0.0438}{(0.0094)(4.896)} = 0.952$$

$$x_K = 1.00 \text{ (assumed)}$$

$$(e) u_A = 290.3 + (0.952)(813.4) = 1064.7 \text{ Btu/lb}$$

$$u_{CO} = 308.7 + (0.675)(798.4) = 847.8 \text{ Btu/lb}$$

$$u_R = 220.6 + (0.72)(867.7) = 845.3 \text{ Btu/lb}$$

$$u_K = 1080.4 \text{ Btu/lb}; h_1 = 1191.7 \text{ Btu/lb}$$

$$h_{2'} = \text{enthalpy of condensate} + \text{heat removed by cooling water per pound of steam condensed}$$

$$= 168.0 + \frac{31,800(63.98 - 33.05)}{1062} = 168 + 926 = 1094 \text{ Btu/lb}$$

$${}_A Q_{CO} = (0.0586)(847.8) - (0.0094)(1064.7) - (0.0492)(1191.7) + 2.54 \\ = 49.70 - 10.00 - 58.70 + 2.54 = -16.46 \text{ Btu} \quad [\text{Eq. (13:7)}]$$

$${}_{CO} Q_R = 0.0586(845.3 - 847.8) + 4.52 = -0.15 + 4.52 = +4.37 \text{ Btu} \quad [\text{Eq. (13:8)}]$$

$${}_R Q_K = (0.0094)(1080.4) + (0.0492)(1094) - (0.0586)(845.3) - 1.09 \\ = 10.15 + 53.85 - 49.50 - 1.09 = +13.41 \text{ Btu} \quad [\text{Eq. (13:9)}]$$

$${}_K Q_A = 0.0094(1064.7 - 1080.4) - 1.33 = -0.15 - 1.33 = -1.48 \text{ Btu} \\ [\text{Eq. (13:10)}]$$

$$(f) Q_{\text{cycle}} = -16.46 + 4.37 + 13.41 - 1.48 = -0.16 \text{ Btu}$$

As indicated by its negative sign, this is the heat flow *to* the atmosphere. As a check, see the calculation to follow.

$$(g) \text{ Work per pound of steam} = \frac{W_e}{J} = \frac{\text{net work of cycle}}{M_f} = \frac{4.65}{0.0492} = 94.5 \text{ Btu/lb}$$

From Eq. (13:4),

$$h_{2'} = 1191.7 - 94.5 = 1097.2 \text{ Btu/lb}$$

Note that this value of  $h_{2'}$  assumes the engine to be an adiabatic engine. The difference between the two values of  $h_{2'}$  is  $1094 - 1097.2 = -3.2 \text{ Btu/lb}$ . Per cycle, this



difference is  $(0.0492)(-3.2) = -0.16$  Btu. Considering that all calculations were made on the slide rule, this check is much closer than was to be expected.

$$(h) \quad \eta_e = \frac{W_e}{J(h_1 - h_2)_s} = \frac{94.5}{1191.7 - 1033} = 0.595 \quad [\text{Eq. (13:5)}]$$

or

$$\eta_e = \frac{h_1 - h_{2'}}{(h_1 - h_2)_s} = \frac{1191.7 - 1097.2}{1191.7 - 1033} = 0.595 \quad [\text{Eq. (13:6)}]$$

Note that here it was necessary to use  $h_{2'}$  as calculated for an adiabatic engine. Equation (13:5) is the basic expression for engine efficiency; Eq. (13:6) is valid only for an adiabatic (though not necessarily a reversible) engine.

**13:8. Reduction of Cylinder Condensation.** It is evident that the loss due to cylinder condensation will vary in magnitude with the mass of metal that is successively heated and cooled per pound of flow steam per cycle and with the extreme variation of temperature of this metal in the course of the cycle. It follows that any steps that are taken with a view toward reducing the effects of cylinder condensation on engine efficiency should operate either to reduce the mass of metal per pound of flow steam or to reduce the interval through which the temperature of the cylinder fluctuates.

The temperature of the cylinder will always lag behind the temperature of the steam it contains so that, while the engine is in operation, the highest temperature reached by the cylinder will never be as high as the temperature of the steam as supplied the engine nor will the cylinder temperature fall as low as that of the exhaust steam. Increasing the difference between the ranges of temperature through which the steam and the metal of the cylinder and piston fluctuate will have a beneficial effect in reducing cylinder condensation losses. Two general methods of lowering the ratio which the extreme fluctuation of cylinder temperature bears to the difference between the limiting temperatures of the steam in the course of the cycle are:

1. Decreasing the time period during which the metal surfaces are exposed to steam at the highest and lowest temperatures of the cycle.

2. Reducing the time rate of heat transfer between steam and metal. The first method may be implemented by either shortening the period of admission and/or the period of exhaust in the cycle to a smaller fraction of the complete cycle or by increasing the speed with which the entire cycle is traversed. With reference to the second method, it has been found that the rate of heat transfer is increased in proportion to the wetness of the cylinder walls and this, in turn, will depend on the percentage of moisture in the steam contained within the cylinder; by supplying steam to the engine highly superheated, the time rate of heat transfer can thus be reduced.

When cutoff takes place at a later point in the power stroke, it might appear from the preceding paragraph that the effect would be to increase the bad effects of cylinder condensation because of the lengthening of the period of admission. This is balanced by the opposing argument that the weight of flow steam per cycle is greater for longer cutoffs and the total effect of the fluctuation of cylinder temperature is less *per pound of flow steam*. Up to a certain limit, therefore, long cutoffs are beneficial in reducing the effects of cylinder condensation on engine efficiency; this limit is often set by the introduction of increasing incomplete-expansion losses by delaying the cutoff.

Some specific measures which have been taken in engine design in the effort to reduce cylinder condensation losses include:

1. *High speed*. While engine speeds do not compare with turbine speeds, there is a considerable variation according to the size of the engine and type of valve used.

2. *Use of superheated steam*. The effect of supplying steam to the engine as superheated steam has been discussed above. The correspondingly higher steam temperatures sometimes require the use of special valves, designed to resist warping.

3. *Corliss valves*. The engine of Fig. 13:1 has valves of the Corliss type. This design provides separate ports for incoming and outgoing steam and reduces the mass of the metal that is alternately heated and cooled in the course of the cycle. Also, the ports are much shorter than in the slide-valve engine, with the same effect in reducing the ratio of the mass of metal to the mass of flow steam.

4. *Multiple expansion*. To carry out the total expansion of the steam in stages, as is so commonly done in the turbine, requires, in the reciprocating engine, a separate cylinder for each stage of the expansion, with correspondingly increased losses due to mechanical friction; therefore the multiple-expansion reciprocating engine is usually built as a compound (two-stage-expansion) engine, although triple- and quadruple-expansion engines are in use. In single-expansion, there are two lags, or intervals, between the temperature of the steam and the temperature of the cylinder; one of these is the temperature interval between the highest temperature at which steam is supplied the cylinder and the somewhat lower peak temperature reached by the metal surfaces; the other is the difference between the temperature of the exhaust steam and the lowest temperature of the cylinder. In the compound engine, there are four such lags, two for each stage of expansion, and the total range of the fluctuation of cylinder temperature is somewhat lessened. Moreover, the high-pressure stage of the expansion is carried out in a smaller cylinder, thus reducing the mass of metal per pound of flow steam per cycle in that stage.

5. *Uniflow design*. The possibility of moving the exhaust valves from



the head of the cylinder has been mentioned previously. In the uniflow engine the exhaust valves are mere slots in the cylinder wall, being placed near the outer end of the piston stroke. These slots are uncovered by the piston near the end of the power stroke, allowing a major portion of the steam to escape from the cylinder; as the piston begins its return stroke, the slots are again closed and the remainder of the charge is compressed. As has been pointed out above, the greater amount of work thus expended on compression is recoverable during the succeeding cycle. A long piston makes it possible to use the same slots, placed at the center of the cylinder, for the exhaust from both ends in double-acting design. The name *uniflow* derives from the fact that the steam enters at one end of the piston stroke and leaves at, or near, the other, thus giving one-way flow; when other types of valves are used, the term *counterflow* is employed to describe the flow of steam through the cylinder. The advantage of the uniflow engine in reducing the effects of cylinder condensation is due to its reduction of the total interval through which the temperature of the cylinder fluctuates; this comes as the result of the shortening of the period of exhaust. This advantage is increased because exhaust steam never *flows* over the surfaces near the admission end of the cylinder and initial condensation effects are especially reduced, thus increasing the quality at cutoff. Uniflow design is quite effective, producing steam rates (pounds of steam used per horsepower-hour or per kilowatt-hour) which are comparable with those obtained by compounding; the uniflow engine is less bulky and less costly than the compound engine.

**13:9. Methods of Governing the Engine.** Both the reciprocating engine and the turbine are usually designed to operate at constant speed under variable load. To adjust the output of the engine to the fluctuating load, some means of controlling the rate at which steam is supplied the engine must be provided; this control is called *governing*.

There are two basic methods of governing an engine or turbine, as already suggested in Art. 11:12 with reference to the governing of the turbine. The first of these is *cutoff governing*. Cutoff governing, as applied to the reciprocating engine, consists in changing the position of cutoff to conform to the load on the engine. This requires the provision of a valve mechanism so designed that the position of cutoff may be altered, usually automatically, while the engine is in operation. Although the engine efficiency may be slightly changed, principally owing to the effect of a change in the valve setting on the incomplete-expansion and cylinder condensation losses, steam is supplied the cylinder at unchanged pressure and the exhaust pressure also remains the same. Thus the maximum work that could be obtained from each pound of flow steam in an equivalent reversible adiabatic engine is not affected.

The second method is called *throttle governing* and consists in control of

engine output by throttling the steam to lower pressure before it enters the steam chest of the reciprocating engine; the position of the valve events is not changed. This has the effect of lowering the top line of the indicator diagram and so reducing the net-work area enclosed. As shown in Fig. 13:6, this method of governing, although it can be used with a valve of simpler and less costly design, is thermodynamically expensive. In the figure, steam is supplied the engine by the boiler at the state which is designated by point 1; as the result of an isentropic expansion to exhaust pressure  $p_2$ , the reversible adiabatic engine could deliver the difference  $h_1 - h_2$ , represented by the length of the line 1-2 in the figure, in the form

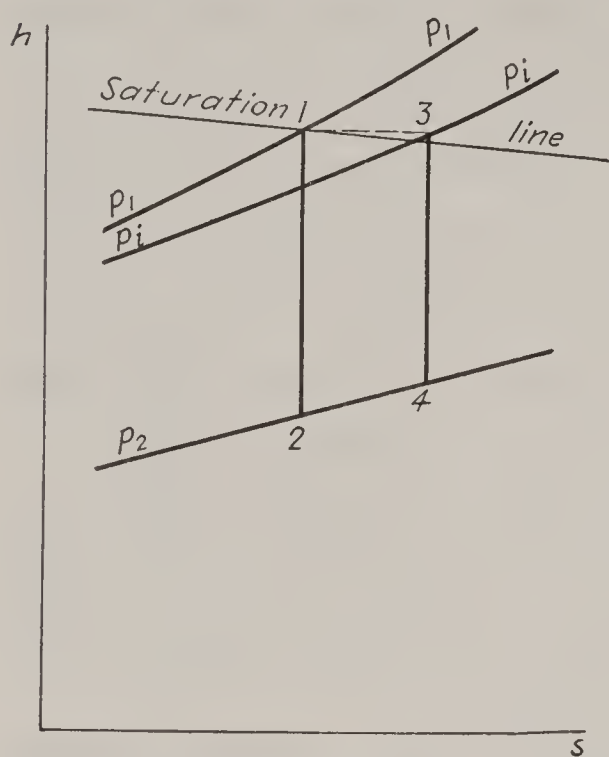


FIG. 13:6. Thermodynamic effect of throttle governing.

of work. Under lighter load, the governor steps in to throttle the steam to a lower pressure  $p_i$  before it enters the cylinder. This does not change the enthalpy of the steam, as we have seen in Chap. 7, but does increase its entropy, and the new supply state is indicated by point 3 of Fig. 13:6. A reversible adiabatic engine, accepting the steam at state 3, could discharge it at the state corresponding to point 4 of the figure, delivering the enthalpy difference  $h_3 - h_4$  in the form of work. This is a less effective use of the energy in the steam than the expansion along line 1-2, as is evident from the figure.

Cutoff governing is thus thermodynamically superior to throttle governing; the same conclusion may, of course, be applied to the governing of turbines.

**13:10. Reciprocating Engine versus Turbine.** The reversible-adiabatic-turbine and the reversible-adiabatic-reciprocating-engine prime movers are alike in the amount of work they can, in theory, deliver under parallel conditions of steam supply and exhaust pressure. The choice between the two types of prime mover must be based on practical factors such as cost, maintenance, adaptability to the conditions under which power is to be delivered, space available, and the percentage of ideal performance that can be realized (the engine or turbine efficiency); this last-named factor will depend on the relative total magnitude of losses such as have been listed for the two types of prime mover.

The turbine must operate at high rotative speeds for high efficiency. This high speed keeps its size, weight, and cost for a given rated power much lower than those of the reciprocating engine and makes it possible to build the turbine in units of a capacity more than ten times greater than



that of the largest practical reciprocating engine. On the other hand, turbines are wasteful of steam in situations where a high starting torque is required and do not retain their efficiency as well as does the reciprocating engine under variable-speed and variable-load conditions. The direction of rotation of the turbine cannot be reversed as is possible for the reciprocating engine in some of its forms.

The thermodynamic losses associated with the reciprocating engine are those due to wiredrawing, to cylinder condensation, to incomplete expansion, and to mechanical friction. In the turbine the flow of steam is steady and continuous and there is, under steady-load conditions, no intermittent opening and closing of valves as in the reciprocating engine; the turbine has no loss comparable with the wiredrawing loss of the engine. Under steady-load conditions, the pressure and temperature at any given point in the steam turbine remain constant; thus there is no fluctuation of temperature and no cylinder condensation loss. The factors which, in the engine, often make it desirable to open the exhaust valve before exhaust pressure is reached by the expanding charge are not present in the turbine; the turbine has no incomplete-expansion loss. Finally, in the turbine there is no need to transform reciprocating into rotary motion; the loss due to mechanical friction is much smaller for the turbine even when gears must be used to reduce its speed.

But the turbine has losses of its own which either are not experienced in engine operation or are much less important in their effect on engine efficiency. These have been discussed in Chap. 11, and the more important may be summarized as:

1. Higher fluid turbulence losses, due to very much greater fluid velocities.
2. Rotation losses, due to rapid movement of blades and rotors.
3. Residual velocity losses, due to unremoved kinetic energy in the steam at exit from the turbine.
4. Leakage around turbine blades, due to clearance between the rotating blades and the turbine casing.

The effect of the characteristic losses associated with the turbine amounts, in total, to much the same deduction from ideal performance as the typical reciprocating-engine losses cause in reducing the performance of the engine. Turbine and reciprocating-engine efficiencies are of the same order and depend primarily on refinement of design. The care and expense which are justified in reducing losses are, in general, a function of the rated power for either type of prime mover. The maximum size in which it is practical to build the reciprocating engine is about 10,000 kw, and a representative efficiency for a reciprocating engine of this capacity is of the order of 80 per cent; in general, about the same efficiency would apply to a turbine unit of 100,000 kw.

## Problems

1. Work Example 13:2A, changing the exhaust pressure to 10 psia.
2. Work Example 13:2B, changing the exhaust pressure to 10 psia.
3. Work Example 13:2B, changing the supply pressure to 200 psia.
4. Work Example 13:2B, changing the clearance to 6 per cent.
5. During a test which is made at constant load, a double-acting engine operates at 140 rpm, receiving saturated steam at 200 psig and exhausting to the atmosphere ( $p = 14.7$  psia). The average indicator card has an area of 3.4 in.<sup>2</sup>, the indicator spring having a scale (the scale of indicator-card ordinates) of 100 psi/in., and the scale of indicator-card abscissas being 0.5 ft<sup>3</sup>/in. The test shows that 1200 lb of steam is supplied the engine during a 15-min period. (a) What is the indicated horsepower at which the test was conducted? (b) What is the engine efficiency based on the indicated horsepower? (c) What is the quality of the steam as it is exhausted from the engine?
6. An engine receives 1000 lb of steam at 240 psia, 98 per cent quality, during a 20-min constant-load test. The condition of the steam in the exhaust line is  $p = 4$  psia,  $x = 0.90$ . Assume an adiabatic engine. (a) What indicated horsepower does the engine develop? (b) What is the engine efficiency?
7. Steam is supplied to an engine at 200 psig as saturated steam. At cutoff, which takes place at 25 per cent of the stroke, the quality is 77 per cent because of initial condensation; the pressure at cutoff is 185 psig, owing to wiredrawing. The piston displacement of the engine is 2 ft<sup>3</sup>, and the clearance is 6 per cent. What weight of H<sub>2</sub>O is present in the cylinder at cutoff? If release takes place at 95 per cent of the stroke and the pressure is 42 psig at release, what is the quality of the steam at release?
8. In Prob. 7, the event of compression is located at 30 per cent of the stroke as read from the indicator card, and the pressure of the steam at that point is scaled from the indicator card as 2 psig. Assuming the steam to be dry at release, what is the weight of cushion steam? The weight of flow steam?
9. In engine design, the designer often approaches the problem by laying out an *ideal*, or *conventional*, *indicator diagram* which is based on the pressures at which steam is supplied and exhausted, a planned cutoff percentage at full load (usually 40 per cent or less), and zero clearance. This ideal card has an appearance similar to Fig. 13:2 except that, since the cutoff percentage has been independently selected, expansion will not be complete and the pressure at the end of the expansion curve which begins at cutoff will be higher than the exhaust pressure. Release is assumed to be located at the end of the power stroke, and the pressure at release is calculated on the assumption that the product  $PV$ , where  $P$  is the absolute pressure, is constant between cutoff and release. Following release, the ideal diagram shows a vertical drop of pressure to exhaust pressure and, following that, a rejection of steam from the cylinder at constant pressure as in Fig. 13:2. Sketch an ideal indicator card, based on supplying saturated steam at 150 psia, exhausting at 3 psia, with cutoff assumed to be at 30 per cent. What is the pressure at release? What is the mean effective pressure shown by this ideal indicator card?
10. Having constructed an ideal diagram as in Prob. 9, the designer applies a *diagram factor* which his experience tells him will approximately express the ratio of the mean effective pressure of the real indicator diagram taken from an engine operating under equivalent conditions to the mep of the ideal diagram. Assuming a diagram factor of 0.80, calculate the indicated horsepower which will be developed by a simple double-acting steam engine of 15 in. bore and 20-in. stroke, with 8 per cent clearance,



operating at 120 rpm. The steam supply and exhaust pressures and the percentage of cutoff are as in Prob. 9.

11. In Prob. 10, assume that the pressure at cutoff is 140 psia and the quality of the steam at that point in the stroke is 0.75. Also assume that compression is at 25 per cent, the pressure at compression is 4 psia, and the steam remaining in the cylinder at compression is dry. What weight of steam is supplied the engine per hour? What is its steam rate (pounds of steam supplied the engine per indicated horsepower-hour delivered)? What is the engine efficiency?

12. An engine is double-acting, 12 in. bore and 15-in. stroke, and operates at 150 rpm. Its clearance is 8 per cent at each end of the cylinder. During a 30-min test at constant load, it is supplied with 1000 lb of saturated steam at 140 psia. The condenser pressure is 14.7 psia. Condensate leaves the condenser at 200°F. Per pound of steam condensed, 35 lb of cooling water passes through the condenser, entering at an average temperature of 70°F and leaving at an average temperature of 96.4°F. Events as shown on the indicator card occur as follows:

Cutoff at 25 per cent, 130 psia.

Release at 95 per cent, 40 psia.

Compression at 30 per cent, 18 psia.

Admission at 0 per cent, 85 psia.

The scale of the indicator spring (the scale of ordinates on the indicator diagram) is 80 psi/in. The length of the indicator diagram (representing the total piston displacement) is 4 in. Areas are measured from the card beneath the lines connecting successive events and above a horizontal line representing the pressure of the atmosphere (14.7 psia) and found to be as listed below. A positive sign indicates that work is done by the steam.

Admission to cutoff, +1.50 in.<sup>2</sup>

Cutoff to release, +1.90 in.<sup>2</sup>

Release to compression, -0.10 in.<sup>2</sup>

Compression to admission, -0.31 in.<sup>2</sup>

What are (a) the weight of cushion steam, based on the usual assumption, (b) the weight of flow steam, and (c) the quality at cutoff? Calculate the amount of heat transfer, and state the direction of its flow between (d) admission and cutoff, (e) cutoff and release, (f) release and compression, and (g) compression and admission. (h) What is the net heat transfer for the cycle? Is this an adiabatic engine? (i) What is the efficiency of the engine? (j) What is the steam rate (pounds of steam supplied per horsepower-hour delivered)?

### Symbols

$g$	acceleration of gravity
$h$	specific enthalpy
$J$	proportionality constant
$M$	mass of a system
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow
$s$	specific entropy
$u$	specific internal energy
$v$	specific volume
$V$	volume; volume of a system
$\bar{V}$	velocity
$W$	rate of work delivery per cycle or per unit time

- $x$  quality of wet steam
- $z$  elevation

*Greek Letters*

- $\eta_e$  engine efficiency

*Subscripts*

- $A$  admission
- $c$  cushion steam
- $CO$  cutoff
- $D$  displacement
- $e$  engine
- $f$  flow steam
- $K$  compression
- $R$  release
- rev reversible
- $s$  constant entropy



## CHAPTER 14

### POWER—VAPOR SYSTEMS

**14:1. The Carnot Cycle as a Vapor Cycle.** It will be remembered that the Carnot cycle requires that heat be supplied at the constant temperature of the source to the working fluid and that the rejection of heat must be at the constant temperature of the refrigerator. Heat exchange at constant temperature has not proved practical when the working substance is a gas or a superheated vapor, and wide variations from the ideal cycle have resulted. But a heat exchange at constant temperature also takes place at constant pressure if the fluid is a *saturated* vapor. In a steady-flow heat exchanger, such as a boiler or a condenser, the pressure of the fluid remains essentially constant as it passes through the unit.<sup>1</sup> Thus one of the objections to the Carnot cycle as a practical cycle is removed. Further, as a steady-flow cycle, it is no longer necessary that the working cylinder act as the heat exchanger; that function can be transferred to devices that are better adapted for the purpose.

In Fig. 14:1, a  $T$ - $s$  diagram, a Carnot cycle has been placed between the saturated liquid and dry-saturated-vapor lines of the vapor which is the working substance. The process 1-2 represents the addition of heat to the vapor; this is carried out in a boiler which, in the cycle illustrated, receives the fluid as a saturated liquid at the temperature  $T_s$  and delivers it at the same temperature (and with no change in pressure) but as a dry and saturated vapor. Since the boiler, as a practical device, operates at essentially constant pressure, line 1-2 is shown in its greatest possible length; in the figure, if point 1 were moved to the left and/or point 2 to the right, the pressures would differ at supply and discharge. The

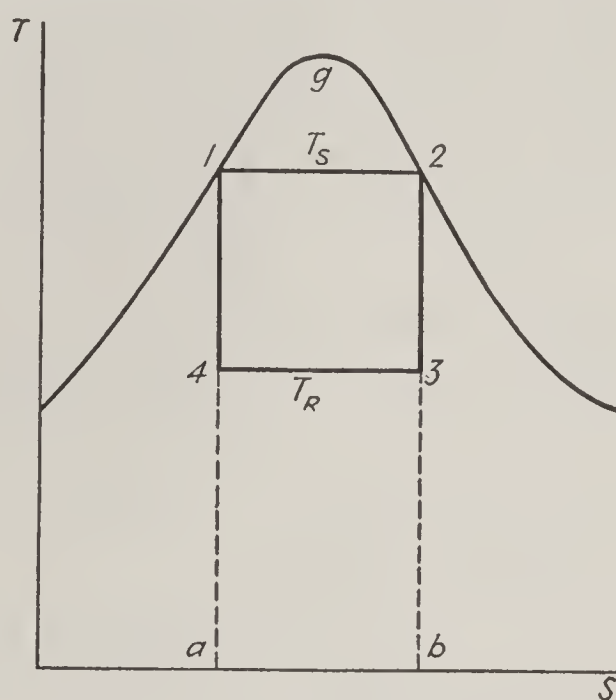


FIG. 14:1. The Carnot vapor cycle.

<sup>1</sup> Because of its viscosity, the real fluid will always show at least a small drop in pressure through the steady-flow heat exchanger, but as rates of flow (velocities) decrease, this differential of pressure necessary to overcome flow resistance approaches zero as a limit.

amount of heat supplied per pound of fluid flow is represented by the area 1-2-*b*-*a*. This heat is supplied during steady flow through the boiler and, neglecting differences in stored energy due to elevation and velocity at entrance to and exit from this unit, may be shown, according to Eq. (3:5), to be equal to the difference of enthalpy at the two stations,  $h_2 - h_1$ .

The rejection of heat represented by process 3-4 takes place in a steady-flow heat exchanger called a condenser and is carried out at the constant temperature  $T_R$  of the refrigerator. Since points 3 and 4 both lie within the saturated-vapor region, this heat is rejected at constant pressure, a practical method of steady-flow heat exchange. The heat rejected per pound of fluid flow in the condenser is represented by area 4-3-*b*-*a* of the

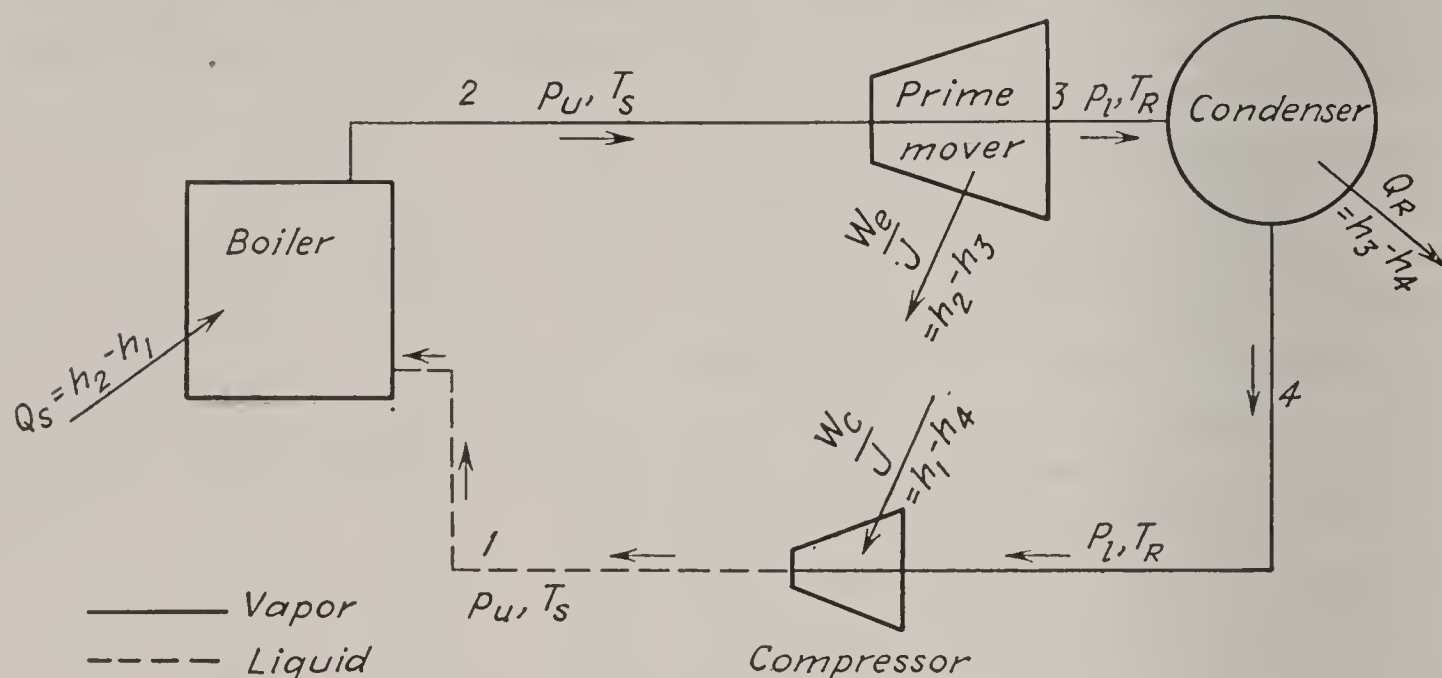


FIG. 14:2. Flow diagram—Carnot vapor cycle.

figure and, again neglecting differences of elevation and velocity at entrance and exit and applying Eq. (3:5), is equal to  $h_3 - h_4$ .

The isentropic expansion process 2-3 is carried out in a reversible adiabatic prime mover which delivers work to external systems in the amount  $h_2 - h_3$  per pound of fluid. A part of this work is returned to drive the reversible adiabatic compressor that is required to close the cycle by carrying out process 4-1; the amount of work so returned is  $h_1 - h_4$ . The flow diagram of the Carnot steady-flow vapor cycle is shown in Fig. 14:2.

Although an examination of the proportions of Fig. 14:1 will show that the efficiency of the Carnot steady-flow vapor cycle is  $(T_S - T_R)/T_S$  and thus the maximum thermodynamically conceivable for a heat engine and although many of the practical difficulties that block the demonstration of the Carnot nonflow cycle have been avoided, the Carnot vapor cycle is still not a practical cycle and is not used as the basis of a real power plant. This is largely because the vapor-compression process 4-1 is difficult to accomplish. This process would require that the fluid be removed from



the condenser before condensation had been completed; because there is no indication in terms of changes in temperature or pressure as to when point 4 has been reached and because, owing to the great difference in their densities, the liquid and the vapor portions of the mixture tend to separate during condensation, the removal of the vapor as a homogeneous mixture at condition 4 is not easily managed. Again, although the ratio of the net work of the cycle to the gross work of expansion is more favorable than when the working fluid is a gas, this ratio still suffers by comparison with the corresponding ratio of vapor cycles to be discussed in following pages of this chapter. The effect of a low work ratio in making a cycle more vulnerable to the irreversibilities of the real engine has been pointed out in Example 4:9.

*Example 14:1.* (a) What is the efficiency of a Carnot vapor cycle in which steam at 600 psia is supplied the prime mover and the condenser pressure is 1 psia? (b) If the fluid is to enter the boiler as a saturated liquid, at what quality must it be withdrawn from the condenser? (c) Assuming that the steam is dry as it enters the prime mover, what amount of work is performed in that unit per pound of steam flow? (d) What amount of work must be returned for compression? (e) What are the net work of the cycle and its ratio to the gross work of expansion?

*Solution:*

(a) The saturation temperatures of steam at 600 and 1 psia are, respectively, 486.21 and 101.74°F. Then

$$\eta = \frac{486.21 - 101.74}{486.21 + 460} = 0.407$$

(b)  $s_4 = s_1 = 0.6720 = s_{f_4} + x_4 s_{fg_4} = 0.1326 + x_4(1.8426)$  or  $x_4 = 0.292$

(c) Reading from the Mollier diagram,  $h_2 = 1203$  Btu and  $h_3 = 807$  Btu. Then

$$\frac{W_e}{J} = h_2 - h_3 = 1203 - 807 = 396 \text{ Btu/lb}$$

(d)  $h_4 = h_{f_4} + x_4 h_{fg_4} = 69.7 + (0.292)(1036.2) = 372.2$  Btu;  $h_1 = 471.6$  Btu

$$\frac{W_c}{J} = h_4 - h_1 = 372.2 - 471.6 = -99.4 \text{ Btu/lb}$$

The negative sign indicates that this work is returned. Note that, having determined the enthalpies  $h_1$ ,  $h_2$ ,  $h_3$ , and  $h_4$ , the efficiency as calculated in part *a* may be checked, as follows:

$$\eta = \frac{Q_S - Q_R}{Q_S} = \frac{(h_2 - h_1) - (h_3 - h_4)}{h_2 - h_1} = \frac{(1203 - 471.6) - (807 - 372.2)}{1203 - 471.6} = 0.407$$

(e) Net work of cycle  $= \frac{W_e}{J} + \frac{W_c}{J} = 396 - 99.4 = 296.6$  Btu/lb

$$\text{Work ratio} = \frac{296.6}{396} = 0.75$$

This answer may be compared with the work ratio calculated in part *d* of Example 4:9 for a Carnot cycle employing a gas as the working substance. Although the temperatures of source and refrigerator are nearly the same in the two examples, the work ratio of the vapor cycle is much more favorable.

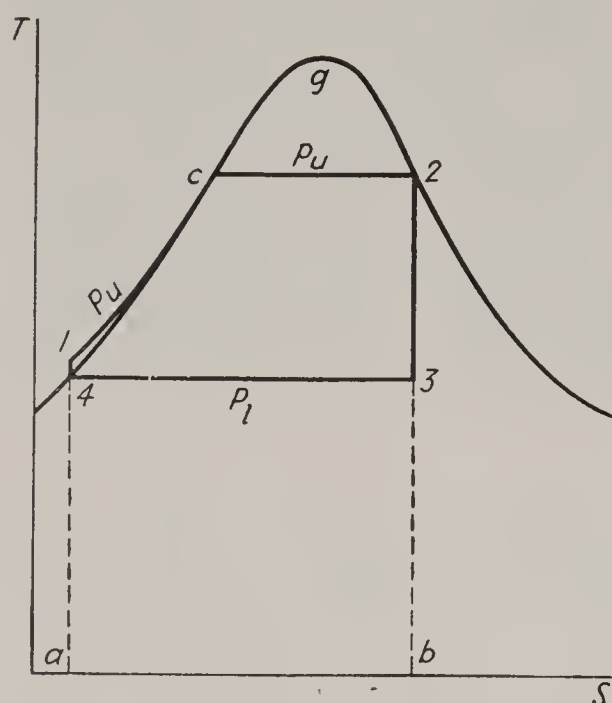


FIG. 14:3. The Rankine cycle.

**14:2. The Rankine cycle** is illustrated on  $Ts$  coordinates in Fig. 14:3. In the Rankine cycle, concessions are made to practicability by specifying that the transfers of heat that take place in the vapor generator (the boiler and, sometimes, the superheater) and the condenser shall be at constant pressure and that the heat-rejection process in the condenser shall continue until condensation is completed, *i.e.*, the fluid exits from the condenser as a saturated liquid. For the limiting temperatures  $T_s$  and  $T_R$  of the Carnot cycle are substituted limiting pressures  $p_u$  and  $p_l$ , respectively,

the upper and lower pressures reached by the fluid in its passage through the cycle. The flow diagram of the Rankine-cycle plant is shown in Fig. 14:4. The boiler receives the fluid as a compressed liquid at the pressure  $p_u$ . As heat is added in that unit, the first effect on the condition of the

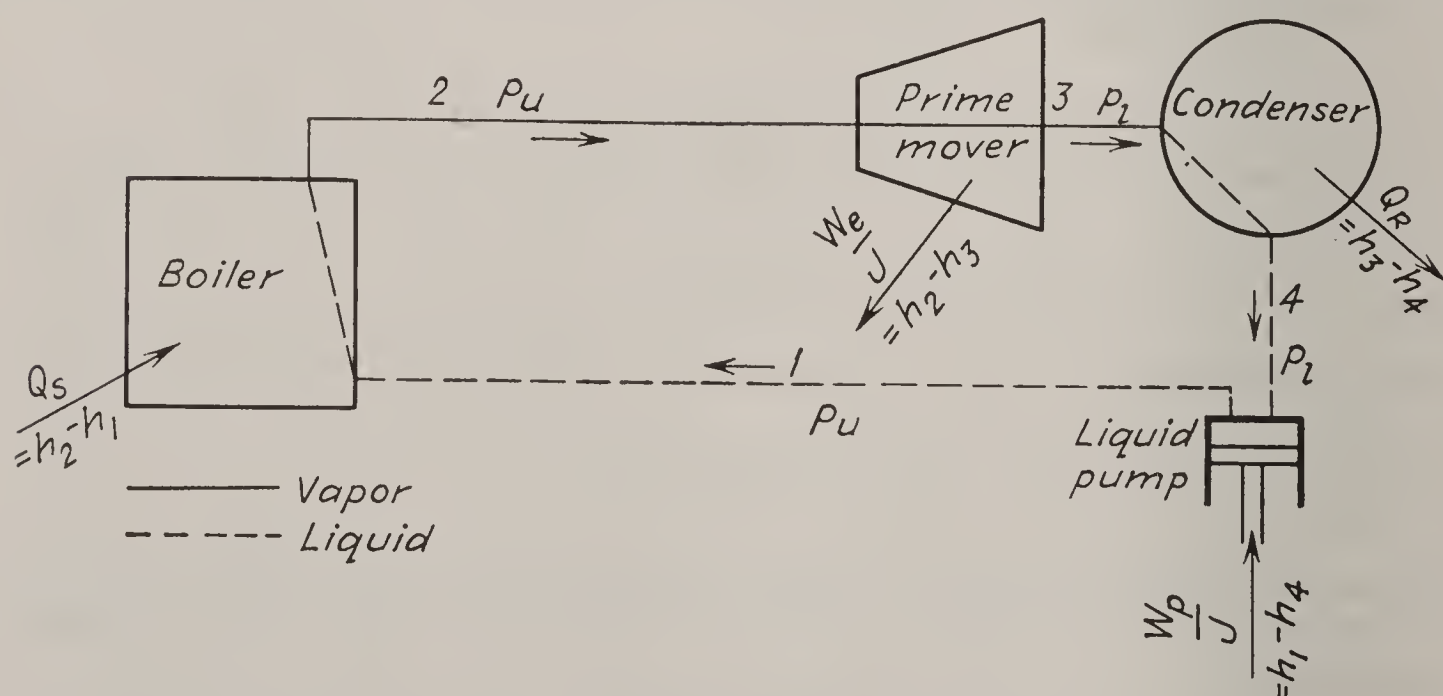


FIG. 14:4. Flow diagram—Rankine cycle.

fluid is to raise the temperature of the compressed liquid (process 1-*c* of Fig. 14:3) until at *c* it has reached the saturation temperature equivalent to the pressure  $p_u$  at which the boiler operates. As further heat is added (process *c*-2), still within the boiler, the liquid evaporates at constant pressure  $p_u$  (and constant temperature) until it leaves the boiler as a dry



saturated vapor at condition 2. The operation that takes place in the boiler is essentially a steady-flow process; the differences in stored energy of the fluid due to differences of elevation and velocity at entrance to and exit from the boiler may be considered negligible, and no external work accompanies the process. Applying Eq. (3:5), it may be shown that

$$Q_s = h_2 - h_1 \quad (14:1)$$

where  $Q_s$  = heat supplied per pound

$h_1$  = specific enthalpy of compressed liquid at entrance to boiler

$h_2$  = specific enthalpy of the vapor as it leaves boiler

Process 2-3 is carried out in a reversible adiabatic prime mover which is identical in type with the corresponding unit employed in the Carnot cycle. As shown in Chap. 11 and 13, the work delivery per pound of fluid flow is

$$\frac{W_e}{J} = h_2 - h_3 \quad (14:2)$$

in which  $h_3$  is the specific enthalpy of the fluid at the same entropy as when it entered the prime mover but at the lower pressure of the cycle,  $p_l$ .

The condenser carries out process 3-4, removing heat from the exhaust vapor until it leaves that unit as a saturated liquid at the lower pressure of the cycle,  $p_l$ . The specific enthalpy at exit,  $h_4$ , may thus be designated, for clarity, as  $h_{f_l}$ . Again the differences in elevation and velocity at entrance and exit from the condenser are inconsiderable, and there is no external work. Applying Eq. (3:5) to this steady-flow heat exchanger, the heat rejected per pound of fluid is observed to be

$$Q_R = h_3 - h_4 = h_3 - h_{f_l} \quad (14:3)$$

in which the use of the subscripts  $f$  and  $l$  indicates that  $h_4$  is the enthalpy of the saturated liquid at the lower pressure of the cycle.

In place of the vapor compressor of the Carnot vapor cycle, the Rankine cycle substitutes a liquid pump (called a feedwater pump in the steam power plant) which receives the fluid as a saturated liquid and compresses it isentropically to the pressure  $p_u$  at which it can enter the boiler to retrace the cycle. This compression is accompanied by a slight rise in temperature (see Chap. 7) which, for purposes of clarity, has been greatly exaggerated in Fig. 14:3. The volume of liquid being small, the (negative) work of this pump, which is a charge against the work output of the prime mover, is very much smaller than that required to drive the vapor compressor of the Carnot vapor cycle, and the work ratio of the Rankine cycle is correspondingly more favorable than that of the Carnot. This makes the efficiency of the cycle less vulnerable to the effects of friction and other irreversibilities in the real power plant. The liquid pump is an

adiabatic device, and, again neglecting differences in elevation and velocity at entrance and exit, the work required to drive it, per pound of liquid flow, can be shown to be

$$\frac{W_p}{J} = h_1 - h_4 = h_1 - h_{f_l} \quad (14:4)$$

Because the liquid is compressible in only very slight degree, its compressibility is customarily ignored and the liquid-pump process is assumed to take place at constant volume. It has been shown previously (see Example 3:6 and Art. 9:8) that the work of steady-flow compression equals  $\int v dP$  per pound of fluid. When compressibility is ignored,  $v$  becomes a constant and the work of the liquid pump, per pound of fluid, may be written as

$$W_p = v_{f_l} \int_l^u dP = (P_u - P_l)v_{f_l} \quad (14:5)$$

in which  $v_{f_l}$  is the specific volume of the saturated liquid at condenser pressure. This expression, its value being more easily computed, is usually substituted for Eq. (14:4). For the conditions usually existing in the real power plant, the error invited is negligible.

The entire cycle of Fig. 14:3 constitutes a heat-engine cycle, and Eqs. (14:1) to (14:5) make it possible to write an expression for its efficiency (which is also, by convention, the thermal efficiency of the prime mover) based on Eq. (2:14) or on Eq. (2:15), as follows:

$$\begin{aligned} \frac{W_{(\text{cycle})}}{J} &= \frac{W_e}{J} - \frac{W_p}{J} = (h_2 - h_3) - (h_1 - h_{f_l}) = h_2 - h_3 - \frac{(P_u - P_l)v_{f_l}}{J} \\ \eta &= \frac{W}{JQ_s} = \frac{(h_2 - h_3) - (h_1 - h_{f_l})}{h_2 - h_1} \\ &= \frac{h_2 - h_3 - (P_u - P_l)v_{f_l}/J}{h_2 - h_{f_l} - \frac{(P_u - P_l)v_{f_l}}{J}} \quad [\text{Eq. (2:14)}] \\ \eta &= \frac{Q_s - Q_R}{Q_s} = \frac{(h_2 - h_1) - (h_3 - h_{f_l})}{h_2 - h_1} \\ &= \frac{h_2 - h_3 - (P_u - P_l)v_{f_l}/J}{h_2 - h_{f_l} - \frac{(P_u - P_l)v_{f_l}}{J}} \quad [\text{Eq. (2:15)}] \end{aligned} \quad (14:6)$$

It will be noted that the Carnot vapor cycle of Fig. 14:1 also operated between limiting pressures  $p_u$  and  $p_l$ , these being the saturation pressures equivalent to the temperatures  $T_s$  and  $T_R$ , respectively. This Carnot cycle is a reversible cycle when the temperatures of the source and of the refrigerator are constant. Under the same conditions, the Rankine cycle is not a reversible cycle for heat must flow downhill during the process



1-*c* of Fig. 14:3, *i.e.*, across a finite interval of temperature. It is only by introducing the concept of a variable-temperature source, as in Chap. 12, that the Rankine cycle may be considered as a reversible cycle so that the advantages that go with plotting it on a  $Ts$  diagram may be fully realized. When this is done, a comparison of the proportionate work and heat-supply areas of Figs. 14:1 and 14:3 (areas 1-2-3-4 and 1-2-*b*-*a* of Fig. 14:1 and areas 1-*c*-2-3-4 and 1-*c*-2-*b*-*a* of Fig. 14:3) will show that, for the same limiting pressures (and thus limiting temperatures), the cycle efficiency of the Rankine cycle will be less than that of the Carnot cycle. Further examination shows that the discrepancy between the efficiencies of the two cycles results from the slope of the saturated-liquid line; if this line were vertical, the Rankine cycle would be identical with the Carnot. A vertical liquid line on the  $Ts$  diagram is a thermodynamic impossibility, for it would mean that the specific heat of the liquid was zero, but a low specific heat of the liquid (in proportion to the heat required for vaporization of the liquid) would increase the proportion which Rankine-cycle efficiency bears to the efficiency of the Carnot under equivalent supply and exhaust conditions. Further study of the two figures brings out the following additional items:

1. The discrepancy between the efficiencies of the two cycles will increase as  $p_u$  is increased and/or  $p_l$  is decreased. This is due to the greater proportion which the heat supplied to raise the temperature of the entering fluid in the Rankine-cycle boiler bears to that required to vaporize it at constant temperature.

2. The efficiency of both cycles will be increased as  $p_u$  is raised. This increase of efficiency will not be directly due to the raising of  $p_u$  but because of the increase in  $T_s$  which accompanies it. But  $T_s$  cannot be increased above the critical temperature of the working fluid ( $T_g$  of Figs. 14:1 and 14:3) without entirely eliminating the efficient addition of heat at constant temperature. The saturated-liquid and saturated-vapor curves of Figs. 14:1 and 14:3 have been located and proportioned on the assumption that water is the working fluid. The possibility of using some more desirable fluid will be discussed later in this chapter.

3. The efficiency of both cycles will be increased as  $p_l$  is lowered. Again, this increase of efficiency will be due directly not to the lowering of  $p_l$  but to the decrease of  $T_R$  which is associated with it. The available refrigerator is the atmosphere, and it is obvious that  $T_R$  cannot be lowered below atmospheric temperature. This sets a lower limit for  $p_l$  which is again based on the pressure-temperature relation of the working fluid.

4. The proportions of Figs. 14:1 and 14:3, when compared, make it evident that the efficiency of the Rankine cycle is, under equivalent supply and exhaust conditions, a quite respectable fraction of the limiting efficiency as set by the Carnot cycle. This proportion of ideal efficiency

is certainly much higher than that for the gas cycles discussed in Chap. 12 (see Fig. 12:3, for example), and it would appear that the Rankine-cycle power plant should operate at much higher efficiency than the internal-combustion power plant. As a matter of fact, the highest efficiencies obtainable in the operation of real vapor power plants based on the Rankine cycle are somewhat below those yielded by the best internal-combustion plants. This results from the use of external combustion in heating the fluid in the Rankine-cycle plant, causing the metallurgical limit to step in to fix the highest temperature that can be attained by the fluid. It has been seen that the source temperature that is available through the process of combustion is between 3000 and 4000°F, while the metallurgical limit for the materials normally used in the construction of boilers is about 1000°F. The temperature  $T_s$  in the Rankine-cycle power plant is thus limited in practice to a much lower level than when internal combustion is employed. In other words, the irreversibility of the vapor plant with respect to the difference between the available temperature of the source and the highest temperature reached by the working fluid is much the greater, and although the Rankine cycle shows a much higher proportion of Carnot-cycle efficiency when compared on the basis of the same  $T_s$ , the comparison is made with a much less efficient Carnot cycle than is the case for the internal-combustion plant. On the other hand, a wider selection of fuels is available for external combustion, and the cost of fuel per Btu of calorific value may accordingly be lower.

5. In Figs. 14:1 and 14:3, condition 2 at exit from the boiler has been shown as a saturated-vapor state. In practice, the vapor usually contains at least a small percentage of the liquid at exit from the boiler so that its quality is slightly less than 1 and point 2 would lie slightly to the left of the position shown in the figures. The efficiency of the Carnot cycle would not be changed by this alteration since the proportion which the work area bears to the heat-supply area remains unchanged though both areas are reduced. The efficiency of the Rankine cycle would decrease slightly because the ratio of heat supplied at constant temperature to total heat supplied is slightly smaller, *i.e.*, the average temperature at which heat is supplied is slightly lower.

*Example 14:2A.* A Rankine cycle, using steam as the working substance, operates between limiting pressures of 600 and 1 psia. The steam enters the prime mover as a saturated vapor. (a) What is the net work of the cycle per pound of steam flowing through the cycle? (b) What is the efficiency of the cycle? (c) What is the moisture percentage in the exhaust steam as it leaves the prime mover?

*Solution:*

$$(a) \ h_4 = h_{f1} = 69.7; \ h_2 = 1203; \ h_3 = 807.$$

[Ex. 14:1]

$$\frac{W_e}{J} = h_2 - h_3 = 1203 - 807 = 396 \text{ Btu/lb}$$



Note that this is the same as for the Carnot-cycle prime mover of Example 14:1.

$$v_4 = v_{f_l} = 0.01614 \text{ ft}^3/\text{lb}$$

$$W_p = (P_u - P_l)v_{f_l} = 144(600 - 1)(0.01614) = 1390 \text{ ft-lb or } 1.8 \text{ Btu/lb.}$$

[Eq. (14:5)]

The net work of the cycle is

$$\frac{W_e}{J} - \frac{W_p}{J} = 396 - 1.8 = 394.2 \text{ Btu/lb}$$

(b) Applying Eq. (14:6) to calculate the cycle efficiency,

$$\eta = \frac{1203 - 807 - 1.8}{1203 - 69.7 - 1.8} = \frac{394.2}{1131.5} = 0.348$$

(c) The condition of the steam as it leaves the prime mover is indicated by the position of point 3, corresponding to a pressure of 1 psia and an enthalpy of 807 Btu. The moisture percentage may be conveniently read from the Mollier chart as 28.8 per cent.

It is sometimes desirable, for practical reasons, to deliver superheated vapor to the prime mover. For example, when a turbine is used as the prime mover, the position of point 3 to the left of the dry-vapor line indicates that there is considerable moisture in the steam jet as it impinges on the blades, and this moisture may be the cause of serious blade erosion, as has been pointed out in Art. 11:12. If point 2 is moved to the right, into the superheat region, point 3 will also move to the right and its new position will indicate that a lower proportion of dense liquid particles is carried in the high-velocity steam jet.

In the Carnot cycle of Fig. 14:1, point 2 cannot move to the right without abandoning the practical requirement that heat be supplied the cycle at constant pressure. On the other hand, in the Rankine cycle it is specified that heat shall be supplied at constant pressure and point 2 of the Rankine cycle, with superheat, will lie as shown in the Rankine cycle of Fig. 14:5. The flow diagram for this cycle is similar to Fig. 14:4 but with the addition of a heat exchanger, called the superheater, between boiler and prime mover. This is necessary since large amounts of superheat cannot be given the vapor while it is in close contact with its liquid. The superheater accepts the vapor from the boiler, or near, state *d*, and process *d*-2, a constant-pressure process, is carried out in that unit, the vapor being discharged as a superheated vapor at state 2. Equation

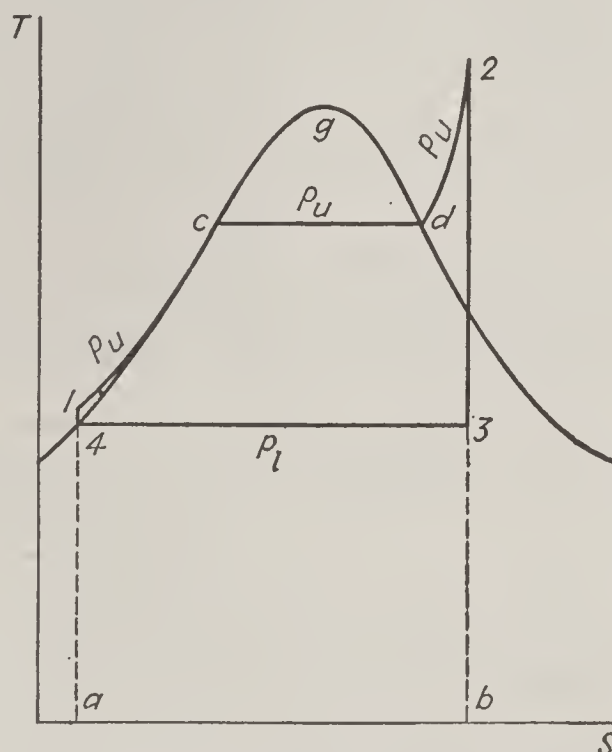


FIG. 14:5. Rankine cycle with superheat.

(14:6) is still valid for the calculation of the cycle efficiency when the change in position of points 2 and 3 is taken into consideration. The movement of state 3 to the right and thus to lower percentages of the liquid in the exhaust vapor will be noted.

A comparison of the proportions of Figs. 14:3 and 14:5, both Rankine cycles having the same limiting pressures  $p_u$  and  $p_l$ , shows that the cycle of Fig. 14:5 will have the higher efficiency and therefore would seem to be the more thermodynamically advantageous. But point 2 cannot lie above the temperature extreme set by the metallurgical limit in either cycle, and a still higher efficiency could have been realized if the heat had been supplied at constant temperature (as to a saturated vapor) at the temperature level reached as the result of the superheating process. Thus the cycle of Fig. 14:5 compares less favorably *with its equivalent Carnot cycle* than does the cycle of Fig. 14:3. When a fluid with a critical temperature which is low as compared with the metallurgical limit, such as steam, is used, the use of superheat may be thermodynamically desirable. Superheat would not be used with fluids having more desirable characteristics than steam in this respect, except for practical reasons such as the damage that may be caused in the turbine prime mover by excessive moisture percentages in the steam.

*Example 14:2B.* The cycle is the same as that of Example 14:2A except that the steam is superheated to 800°F before it enters the turbine prime mover. Answer the same questions that are asked in that example.

*Solution:*

(a)  $h_4 = 69.7$  Btu and  $W_p/J = 1.8$  Btu as in Example 14:2A. From the Mollier chart,  $h_2 = 1408$  Btu, and  $h_3 = 914$  Btu.

$$\frac{W_e}{J} = 1408 - 914 = 494 \text{ Btu/lb}$$

$$\text{Net work of cycle} = 494 - 1.8 = 492.8 \text{ Btu/lb}$$

$$(b) \eta = \frac{1408 - 914 - 1.8}{1408 - 69.7 - 1.8} = \frac{492.2}{1336.5} = 0.368$$

This efficiency is higher than that of the Rankine cycle of Example 14:2A. However, that cycle compared with a Carnot cycle having an efficiency of 0.407 (see Example 14:1), whereas the efficiency of the cycle of this example should logically be compared with that of a Carnot cycle to which heat was supplied at 800°F; the corresponding Carnot cycle efficiency would be  $(800 - 101.74)/(800 + 460) = 0.555$ .

(c) The moisture percentage in the steam as it leaves the prime mover may be read from the Mollier chart at state 3 and is found to be about 18.5 per cent. This is an improvement over the corresponding result in Example 14:2A if the prime mover is of the turbine type.

**14:3. The Reheat Cycle.** The maximum percentage of moisture that is considered permissible in the exhaust steam, if excessive blade erosion is to be avoided when a turbine is the prime mover, is about 10 per cent.



The discussion of Art. 14:2 has indicated that it is advantageous to operate at as high an upper pressure  $p_u$  of the Rankine cycle as is possible considering the pressure-temperature relation of the fluid and its critical temperature. For water, the critical temperature is 705°F at a critical pressure of 3206 psia, and let us suppose, for the purpose of illustration, that it is decided to supply steam to the turbine as superheated steam at a pressure of 2600 psia and a temperature (fixed by the metallurgical limit) of 1000°F. Reference to the Mollier diagram for steam shows that this corresponds to an enthalpy  $h_2$  (Fig. 14:5) of 1456 Btu. We shall further assume that the exhaust pressure is 1 psia, corresponding to a saturation temperature of about 102°F and conforming approximately with the usual practice in the large central-station power plant. The Mollier

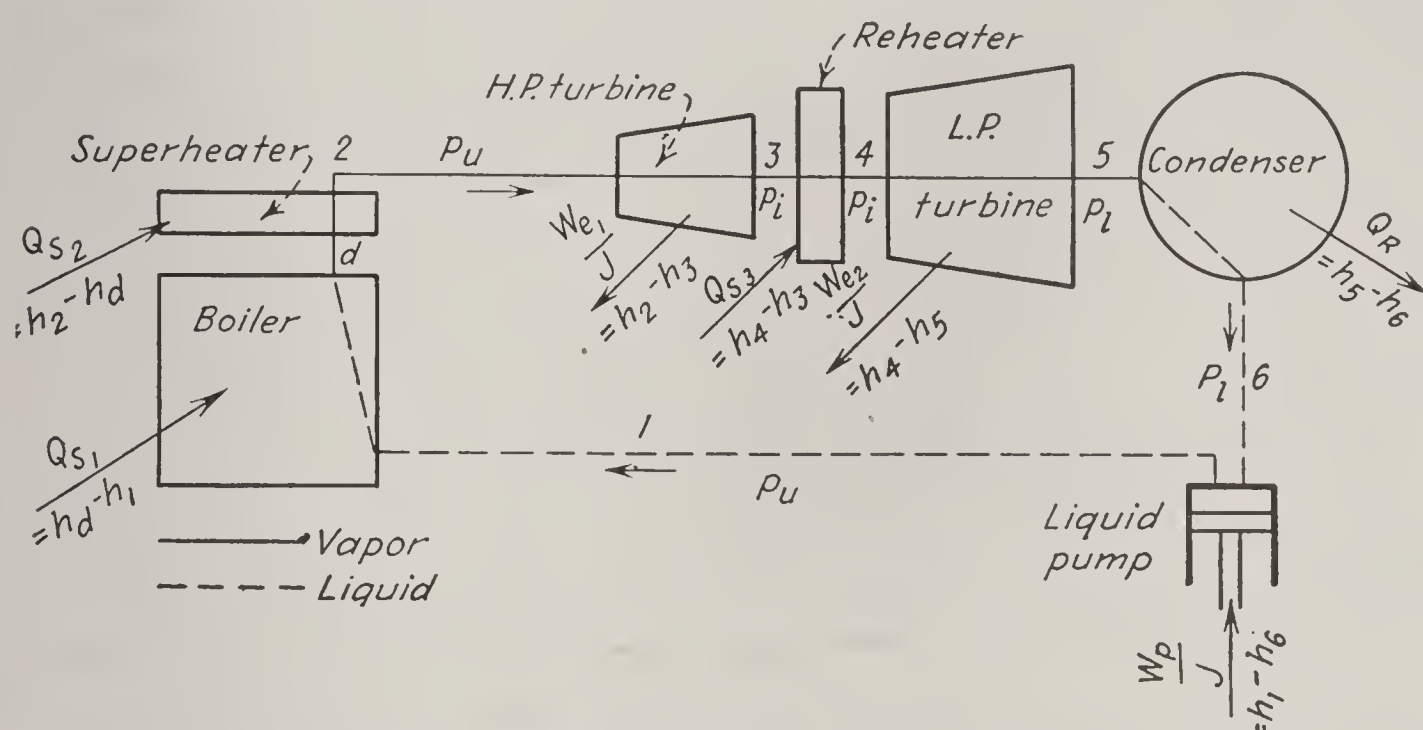


FIG. 14:6. Flow diagram—reheat cycle.

chart shows that state 3, at the end of an isentropic expansion to this exhaust pressure, is identified as having an enthalpy  $h_3$  of 850 Btu and a moisture percentage of nearly 25 per cent. Allowing for an assumed turbine efficiency of 85 per cent, this enthalpy would be increased to  $1456 - 0.85(1456 - 850) = 941$  Btu, which, at 1 psia, corresponds to a moisture proportion of 16 per cent. This is still a higher moisture percentage than is considered permissible, and it appears that we must content ourselves with the lower cycle efficiency that goes with lower steam-supply pressure. After a number of trial calculations, carried out in a manner similar to that used above, we find that if  $p_u = 1200$  psia and steam is supplied the turbine at that pressure and superheated to the metallurgical limit of 1000°F,  $h_2 = 1499$  Btu,  $h_3$  (at the end of isentropic expansion to 1 psia) = 911 Btu, and, again assuming a turbine efficiency of 85 per cent, the enthalpy of the exhaust steam is  $1499 - 0.85(1499 - 911) = 999$  Btu, corresponding to a moisture percentage of about 10

per cent. It thus appears that a limit is set on the attainment of higher efficiency through raising the upper pressure of the Rankine cycle by the necessity of avoiding excessive blade erosion when the turbine is used as the prime mover. Since the turbine is the accepted type of prime mover for the large central-station plant, this is a serious limitation; the *reheat cycle* is used to avoid it.

The flow diagram of the reheat cycle is shown in Fig. 14:6. The boiler and superheater operate at the upper pressure  $p_u$  of the cycle, which may exceed the limit of 1200 psia calculated above. The first stage of expansion is carried out in the high-pressure turbine, which expands the steam

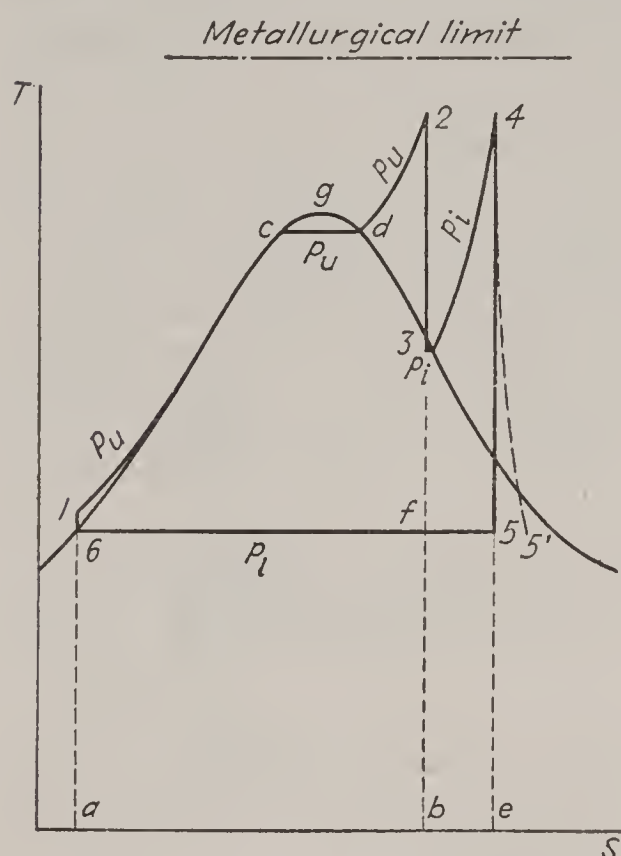


FIG. 14:7. The reheat cycle.

to some intermediate pressure  $p_i$  at which the moisture that has accumulated has not exceeded the allowable limit. The steam exhausted from this unit then enters the reheater (essentially a superheater in its design features) and is brought up to as high a temperature as is practical before further expansion in the low-pressure turbine to final exhaust pressure  $p_l$ . The ideal reheat cycle is shown on  $T$ - $s$  coordinates in Fig. 14:7. If the initial expansion had been carried through, without reheating, the final quality of the steam would have been as at point  $f$  of this diagram. Because of reheat, the state of the exhaust steam shifts to point 5, corresponding to a lower percentage of moisture.

A comparison of Figs. 14:6 and 14:7 shows that, per pound of fluid flow, the heat supplied in the boiler and superheater is  $h_2 - h_1 = h_2 - h_{f_l} - \frac{(P_u - P_l)v_{f_l}}{J}$ .  $Q_s$  will also include the additional heat supplied in the process carried out in the reheater, which amounts to  $h_4 - h_3$ . The heat  $Q_R$  rejected through the action of the condenser, which carries out process 5-6, is  $h_5 - h_6 = h_5 - h_{f_l}$ . The work of the high-pressure turbine is  $h_2 - h_3$ , and that of the low-pressure turbine is  $h_4 - h_5$ . The work that must be supplied to drive the feedwater pump is  $(P_u - P_l)v_{f_l}$ . Based on Eq. (2:14),

$$\eta = \frac{W}{JQ_s} = \frac{(h_2 - h_3) + (h_4 - h_5) - \frac{(P_u - P_l)v_{f_l}}{J}}{\left(h_2 - h_{f_l} - \frac{(P_u - P_l)v_{f_l}}{J}\right) + (h_4 - h_3)} \quad (14:7)$$



The efficiency of the reheat cycle will be found to agree quite closely with the efficiency of the simple Rankine cycle formed by continuing the original expansion to the final exhaust pressure (cycle 1-*c-d-2-f-6* of Fig. 14:7), but it avoids the high moisture percentages in the exhaust steam of that cycle. While the use of reheat does not in itself materially increase the efficiency of the cycle, it enables the use of higher steam-supply pressures and thus the employment of a more efficient cycle.

**Example 14:3.** Steam is supplied the high-pressure turbine of a reheat-cycle plant at 2600 psia, 900°F. After expansion in that unit to a pressure of 400 psia, the steam is reheated to 900°F and expands in the low-pressure turbine to a final pressure of 1 psia. (a) What is the efficiency of the cycle? Compare this efficiency with that of the Rankine cycle which is produced by continuing the original expansion to the condenser pressure of 1 psia (to point *f*). (b) What are the moisture percentages in the steam as it leaves the final stages of the turbine prime mover in each case? (c) Allowing for an efficiency of the low-pressure turbine of 85 per cent, what is the moisture percentage at this point in the reheat cycle?

*Solution:*

(a) The notation is that of Fig. 14:7. From the Mollier diagram,  $h_2 = 1384$  Btu;  $h_3 = 1192$  Btu;  $h_f = 821$  Btu;  $h_4 = 1470$  Btu;  $h_5 = 964$  Btu.

$$x_3 = 0.983; x_f = 0.725; x_5 = 0.863$$

From the tables,  $h_6 = h_{f1} = 69.7$  Btu and  $v_6 = v_{f1} = 0.01614$  ft<sup>3</sup>/lb.

$$\text{Pump work} \leftarrow W_p = (P_u - P_l)v_{f1} = 144(2600 - 1)(0.01614) = 5820 \text{ ft-lb, or } 7.5 \text{ Btu/lb}$$

Applying Eq. (14:7) to calculate the efficiency of the reheat cycle,

$$\eta = \frac{(1384 - 1192) + (1470 - 964) - 7.5}{(1384 - 69.7 - 7.5) + (1470 - 1192)} = \frac{690.5}{1584.8} = 0.435$$

The efficiency of the Rankine cycle, without reheat, is, from Eq. (14:6),

$$\eta = \frac{1384 - 821 - 7.5}{1384 - 69.7 - 7.5} = \frac{555.5}{1306.8} = 0.425$$

It will be noted that the difference between the efficiencies of these two cycles is not large.

(b) As the result of isentropic expansion, the moisture percentages read from the Mollier chart are 13.7 and 27.5 per cent for the reheat cycle and the Rankine cycle, respectively.

(c) The enthalpy at the end of expansion in a real low-pressure turbine which has a turbine efficiency of 85 per cent will be designated as  $h_{5'}$ . Then  $h_{5'} = 1470 - 0.85(1470 - 964) = 1040$  Btu, and this enthalpy corresponds, at a pressure of 1 psia, to a moisture percentage of 6.4 per cent. This is less than the permissible limit of 10 per cent.

**14:4. The Regenerative Vapor Cycle.** The Rankine cycle, without superheat, has an efficiency less than that of the equivalent Carnot solely because of the lower average temperature at which heat is received from

the source during the process of heating the liquid to saturation temperature. This is somewhat the same problem that was encountered in the Stirling cycle discussed in Art. 4:10, and it will be remembered that the efficiency of that cycle was raised to equal that of the equivalent Carnot by employing the principle of regeneration, *i.e.*, by removing heat from the working fluid during one of the processes of the cycle and utilizing this heat to accomplish the rise in temperature required during a later process of the cycle; thus the heat from the source may be supplied at constant temperature, and the cycle may attain the maximum conceivable efficiency, that associated with the Carnot cycle.

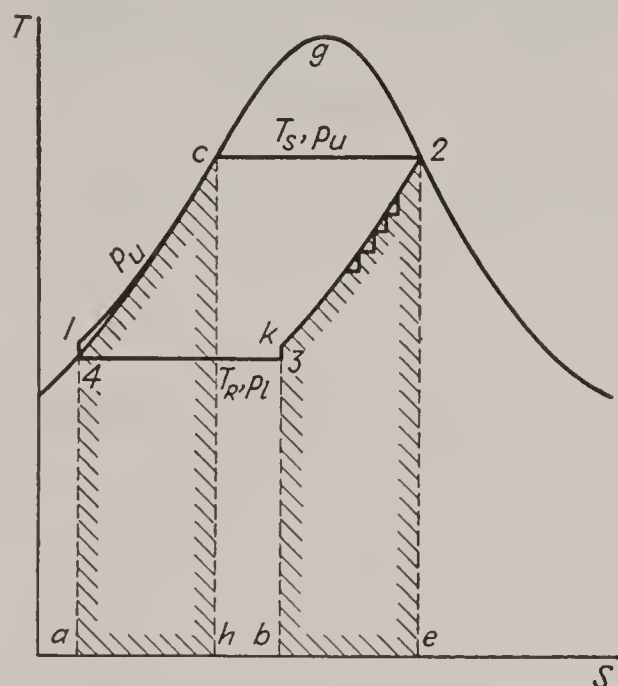


FIG. 14:8. Regenerative vapor cycle (without superheat).

The regenerative vapor cycle applies regeneration to the liquid-heating process (1-c of Fig. 14:3). The heat necessary to accomplish this rise in temperature of the liquid is removed from the vapor during its expansion through the prime mover. The resulting cycle, as it appears when a saturated vapor is supplied the prime mover,<sup>1</sup> is presented in Fig. 14:8. In this figure, the crosshatched area 2-k-b-e represents the heat removed from the expanding vapor and used to supply the heat, represented by area 1-c-h-a, necessary to

preheat the liquid to vaporization temperature; these areas will later be shown to be equal and to have the same shape.<sup>2</sup>

<sup>1</sup> The regenerative vapor cycle, for reasons to be advanced later, is best applied to plants in which the turbine is the prime mover. As has been brought out above, superheated vapor is usually supplied the turbine prime mover for practical reasons, and this introduces a second irreversibility due to the addition of heat to the working fluid at variable temperature during the superheating process. In order to concentrate attention on the regenerative heating of the liquid, the cycle here discussed does not employ superheat. However, the regenerative-liquid-heating principle may be applied to the cycle even when the vapor is supplied the turbine as a superheated vapor, although, in that case, a cycle efficiency equal to that of the equivalent Carnot cycle cannot, even in theory, be realized.

<sup>2</sup> To prove that line 2-k parallels line 1-c, it is necessary only to show that the slopes of these lines are everywhere the same at the same temperature. In the ideal regeneration that is here supposed, the differential of temperature between the vapor which yields the heat and the liquid which receives it is infinitesimal. If this infinitesimal differential of temperature is to be maintained throughout the length of the counter-flow regenerative heat exchanger, the transfer of a small quantity of heat  $\partial Q$  from vapor to liquid must be accompanied by a decrease of vapor temperature  $(dT)_V$  which is equal to the increase of liquid temperature  $(dT)_L$ , or  $(dT)_V = -(dT)_L$ . Let us examine the effect on the entropy of the vapor and of the liquid of the transfer



The heat  $Q_S$  received from the source is thus reduced from that required in the Rankine cycle of Fig. 14:3 to area  $c-2-e-h$ , and  $Q_R$ , discharged to the refrigerator, is represented by area  $4-3-b-a$ . Because the crosshatched areas are the same shape, the widths of the  $Q_S$  and  $Q_R$  areas are the same and their magnitudes are proportional to the temperatures  $T_S$  and  $T_R$ , as in the Carnot cycle; thus the efficiency of the regenerative cycle 1- $c$ -2- $k$ -3-4 is that of the Carnot cycle which operates between the temperatures  $T_S$  and  $T_R$ .

The idealized flow diagram of a vapor power plant to operate on the cycle of Fig. 14:8 is shown in Fig. 14:9. The liquid pump removes saturated liquid at  $p_l$  and  $T_R$  from the condenser and raises its pressure

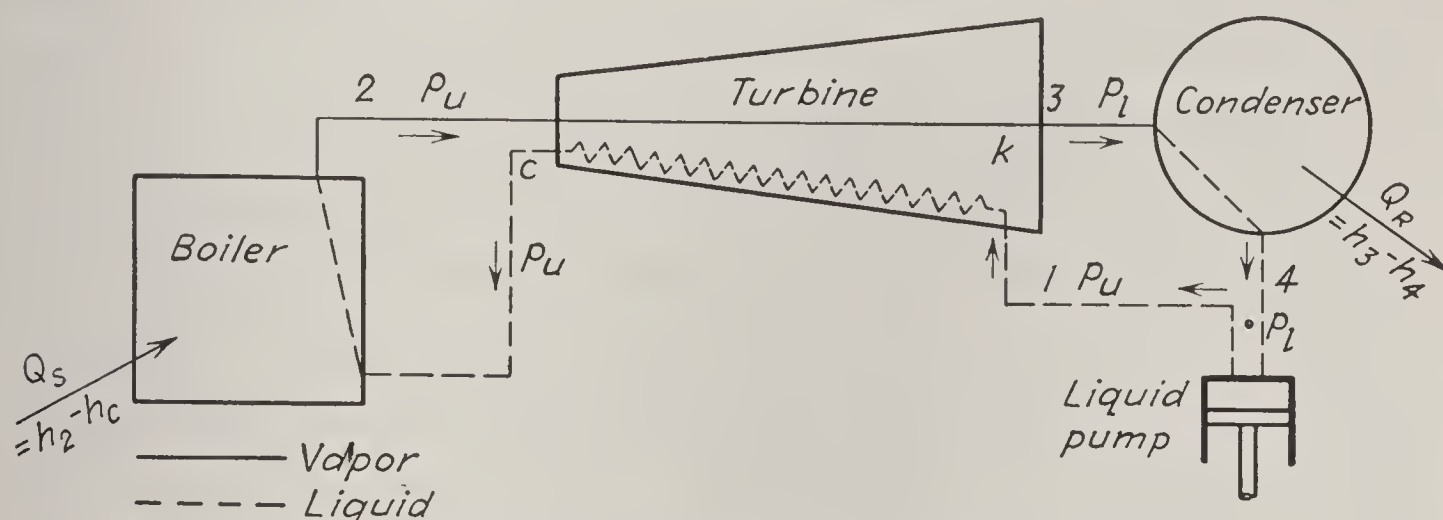


FIG. 14:9. Idealized flow diagram—regenerative vapor cycle.

to  $p_u$ . The temperature is also raised slightly owing to the compression of the liquid, and the liquid goes through process 4-1 of Fig. 14:8. After leaving the pump, the liquid passes through the turbine in a direction opposite to that of the flow of vapor through that unit. Thus a counter-flow heat exchange is made possible, and the liquid issues at the high-pressure end of the turbine at the temperature  $T_S$ ; this is process 1- $c$  of Fig. 14:8. The liquid then enters the boiler as a saturated liquid and evaporates at constant temperature (process  $c$ -2) in that unit as it receives heat, in this case from the source. The expansion of the vapor in the turbine is no longer isentropic, as it is giving up heat to the liquid for the purposes of regeneration, and the expansion line 2- $k$  moves to the left,

of this element of heat. For the liquid, heated at constant pressure, we may write  $(\partial Q)_L = c_{pL}(dT)_L$  and  $ds_L = \frac{(\partial Q)_L}{T} = c_{pL} \frac{(dT)_L}{T}$ , from which the slope of the liquid line 1- $c$ , representing the liquid-heating process on the temperature-entropy diagram, is  $\left(\frac{dT}{ds}\right)_L = \frac{T}{c_{pL}}$ . For the vapor,  $(\partial Q)_V = -(\partial Q)_L = -c_{pL}(dT)_L = c_{pL}(dT)_V$ . Then  $ds_V = \frac{(\partial Q)_V}{T} = \frac{c_{pL}(dT)_V}{T}$ , and the slope of the vapor line 2- $k$  on the  $Ts$  diagram is  $\left(\frac{dT}{ds}\right)_V = \frac{T}{c_{pL}} = \left(\frac{dT}{ds}\right)_L$ . Note that if lines 1- $c$  and  $k$ -2 are parallel, as has here been shown, the heat-exchange areas must have the same shape and size.

paralleling line 1-*c*.\* The very last stage of expansion in the turbine (*k* to 3) is isentropic, for it will be remembered that the liquid pump has raised the temperature of the liquid slightly above  $T_R$  before it entered the turbine for counterflow regeneration.

The reader may form a mental picture of the regenerative heat exchanger of Fig. 14:9 as consisting of liquid-carrying tubes which are embedded in the turbine casing and in the walls of the turbine nozzles. This is an entirely impractical arrangement; instead, in the real steam power plant that operates with regenerative feedwater heating, the heating of the feedwater is accomplished by steps or stages. In Chap. 11, it has been shown that, if desired, some of the steam may be withdrawn from the turbine at the end of any turbine stage. In regenerative feedwater heating as applied in practice, the extracted steam is conducted to a heat exchanger, where it is brought into contact with the feedwater and, as it condenses, raises the temperature of the water as the latter flows toward the boiler. The pressure of the steam remains constant during condensation and therefore, if the steam is saturated as it enters the heater, the condensation process is represented by a horizontal line on the temperature-entropy diagram. If a large number of extraction points (a separate heater is required for each) are selected, line 2-*k* becomes a series of small steps as indicated in Fig. 14:8. The horizontal section of a step represents the condensation of steam in a feedwater heater, the vertical section the isentropic expansion of the steam in the turbine between bleeding points. As the number of extraction points is increased, the stepped expansion line approaches the smooth line 2-*k* in contour. In practice, the number of extraction points (and therefore of heaters) may be one to five or six, depending upon the complexity of design which is justified. Although the cycle efficiency increases with the number of heaters, the gain in efficiency that is produced by the addition of another extraction point becomes less and less with each addition; in the meantime, practical factors, such as equipment cost, fixed charges, and maintenance expense, are increasing and ultimately have the effect of canceling the theoretical gains.

The flow diagram for a three-heater installation is shown in Fig. 14:10; again, for simplicity, steam is furnished the turbine of the plant as saturated steam. The extraction points in the flow of steam through the turbine are *m*, *n*, and *o* and, in practice, must fall between turbine stages; their best location from a thermodynamic viewpoint will be discussed later. From each extraction point, the steam is led to a corresponding heater, in which, as it condenses, it gives up heat to the feedwater. The unextracted portion of the steam continues to expand through the lower pressure stages of the turbine and finally reaches the condenser, to be

\*For footnote see pages 340 and 341.



there condensed into a saturated liquid. This liquid, in the flow arrangement shown in the figure (other pump arrangements are possible and constitute slight variations from this cycle), is pumped from the condenser and raised to boiler pressure  $p_u$  by the feedwater pump. Instead of going directly to the boiler, the feedwater passes through the heaters  $H_o$ ,  $H_n$ , and  $H_m$  in that order (the reverse of the order in which steam has been extracted from the turbine). An increment of heat is added to the feedwater in each heater, bringing its temperature, in the limit, up to the temperature of the condensing steam in that heater and thus to the saturation temperature equivalent to the pressure at the respective extraction point. The amount of steam extracted to each heater is automatically

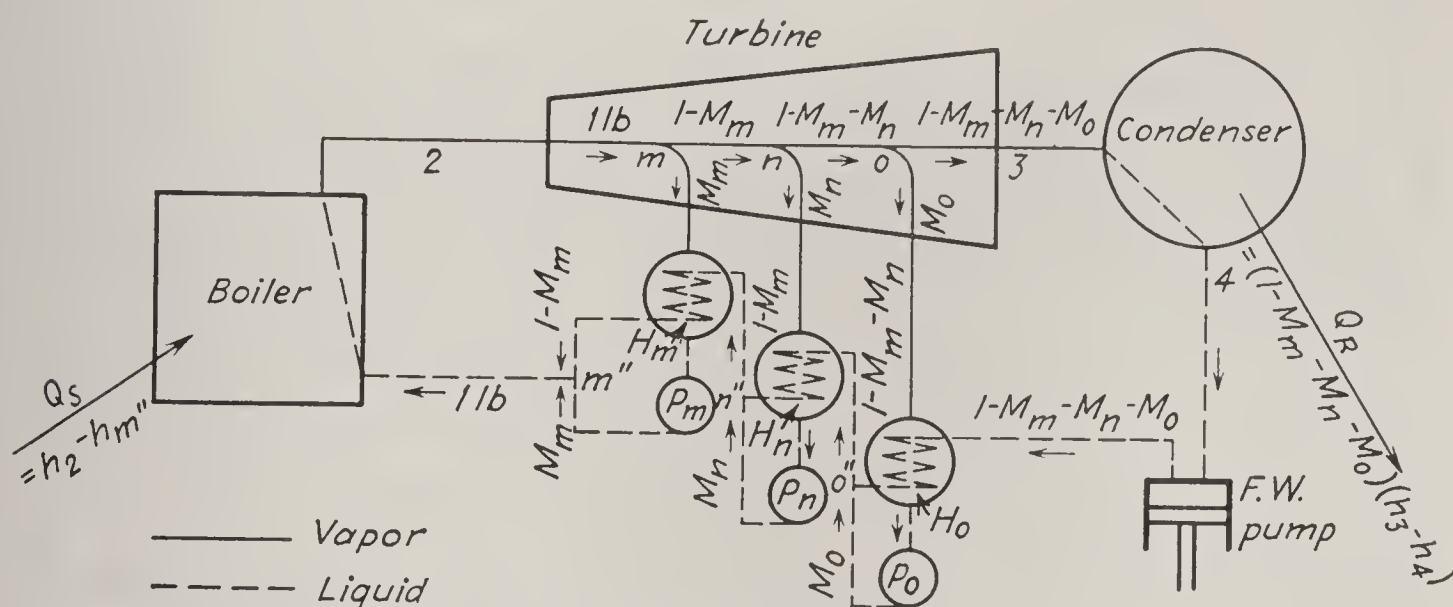


FIG. 14:10. Flow diagram—three-heater regenerative vapor cycle.

controlled by the condensation within that heater, since any condensation will lower the pressure within the heater and thus furnish the pressure differential necessary to draw in an additional supply of steam. It is therefore adjusted according to the heat given up to the feedwater as the latter passes through the heater. A trap is placed below each heater, permitting only condensate to leave the heater; this condensate is picked up by a pump and raised to supply pressure  $p_u$  to join the feedwater at a point beyond the heater. In the limit, the temperatures of condensate and feedwater are the same at this junction, and no irreversibility is caused by the mixing of the two streams.

The temperature-entropy diagram for this three-heater cycle is shown in Fig. 14:11. The saturated-liquid and dry-vapor lines have been shown on this diagram for 1 lb of steam entering the turbine. The entire pound of steam expands isentropically to the first extraction point  $m$ . The process  $m-m'$  of the figure represents the constant-pressure condensation of  $M_m$  lb of extracted steam, which takes place in heater  $H_m$ . The location of  $m'$  is fixed by the sum of the entropies of the condensate resulting from the condensation of the extracted steam and that of the portion of

the original pound which continues its flow through the turbine; their combined weights are 1 lb. The balance of the steam, weighing  $1 - M_m$  lb per pound of steam entering the turbine, continues its isentropic expansion to the second extraction point  $n$ , where a weight  $M_n$  is extracted to heater  $H_n$  and is condensed therein, accounting for process  $n-n'$ ; the same procedure is followed at each extraction point.

Returning to heater  $H_m$ , the feedwater enters this heater at, in the limit, a temperature corresponding to the saturation temperature at the second extraction point, having been raised to that temperature in heater  $H_n$ . It is raised, in heater  $H_m$ , to  $T_m$ , and this feedwater-heating process

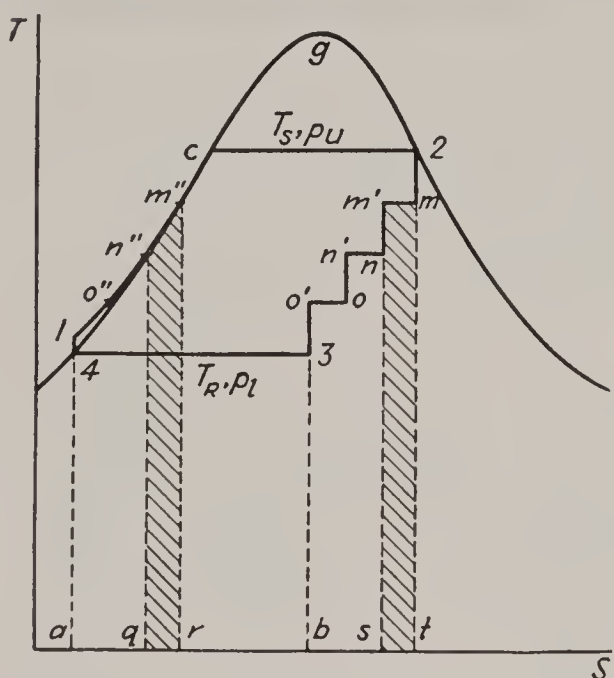


FIG. 14:11. Three-heater regenerative vapor cycle.

is represented in Fig. 14:11 by line  $n''-m''$ . The heat required for this process is represented by area  $n''-m''-r-q$  of the figure and is equal to the heat given up through the condensation of extracted steam in heater  $H_m$ , or area  $m'-m-t-s$ . These two areas therefore represent the regenerative heat exchange as far as heater  $H_m$  is concerned. Similar paired area strips may be located for each heater in the series. These regenerative transfers of heat are irreversible because of the increase of temperature of the feedwater, but the degree of their irreversibility is less than if the heat had been supplied by

the source at the higher temperature  $T_s$ . The efficiency of the cycle will therefore lie between those of the equivalent Rankine and Carnot cycles.

In order to calculate the efficiency of the cycle of Figs. 14:10 and 14:11, it is necessary to know the respective weights extracted at points  $m$ ,  $n$ , and  $o$ . It has been explained above that these weights are automatically adjusted to the requirements of feedwater heating or, in other words, that the heat yielded by the condensing vapor in the heater equals the heat absorbed by the feedwater. By an application of Eq. (3:5), it may be shown that the heat given up by the vapor is equal to its decrease of enthalpy and that the heat absorbed by the liquid is identical with its increase in the same property. Using heater  $H_m$  as an example, the weight of steam condensed is  $M_m$ , its specific enthalpy entering the heater being  $h_m$ , the enthalpy at the end of an isentropic expansion from point 2 to the pressure  $p_m$  at the extraction point; this can be conveniently determined by graphical projection on the Mollier diagram. The specific enthalpy of the extracted steam at exit from the heater, as a saturated liquid at pressure  $p_m$ , may be denoted as  $h_{f_m}$  and can be read from the



tables. The weight of feedwater passing through the heater is  $1 - M_m$  (see Fig. 14:10), and its specific enthalpy at entrance is  $h_{f_n} + \frac{(P_u - P_n)v_{f_n}}{J}$ , in which the second term represents the effect of the feedwater pump on the enthalpy, in raising the pressure above the saturation pressure. Similarly, the specific enthalpy of the feedwater at exit from the heater is  $h_{f_m} + \frac{(P_u - P_m)v_{f_m}}{J}$ . Equating the heat given up by the extracted steam to that received by the feedwater, we may write

$$M_m(h_m - h_{f_m}) = (1 - M_m) \left( h_{f_m} + \frac{(P_u - P_m)v_{f_m}}{J} - h_{f_n} - \frac{(P_u - P_n)v_{f_n}}{J} \right) \quad (14:8)$$

In this equation, once the extraction points have been selected, all terms may be independently evaluated with the exception of the weight of steam extracted; thus  $M_m$  may be computed. In practice, the terms representing the effect of feedwater-pump work on the enthalpy are relatively small and, since they add considerably to the complications of solution without materially changing the final result, are usually dropped. Thus Eq. (14:8) is customarily written in the form

$$M_m(h_m - h_{f_m}) = (1 - M_m)(h_{f_m} - h_{f_n})$$

or

$$M_m = \frac{h_{f_m} - h_{f_n}}{h_m - h_{f_n}} \quad (14:9)$$

A similar analysis to obtain the weight extracted to the second heater is as follows:

$$M_n(h_n - h_{f_n}) = (1 - M_m - M_n)(h_{f_n} - h_{f_o})$$

or

$$M_n = \frac{(1 - M_m)(h_{f_n} - h_{f_o})}{h_n - h_{f_o}} \quad (14:10)$$

By substituting the value of  $M_m$ , as expressed in Eq. (14:9), in this equation, it may be changed to the form

$$M_n = \frac{h_m - h_{f_m}}{h_m - h_{f_n}} \frac{h_{f_n} - h_{f_o}}{h_n - h_{f_o}} \quad (14:11)$$

Proceeding in a similar manner, it may be shown that

$$M_o = \frac{(1 - M_m - M_n)(h_{f_o} - h_{f_3})}{h_o - h_{f_3}} = \frac{h_m - h_{f_m}}{h_m - h_{f_n}} \frac{h_n - h_{f_n}}{h_n - h_{f_o}} \frac{h_{f_o} - h_{f_3}}{h_o - h_{f_3}} \quad (14:12)$$

In substitution in Eqs. (14:9) to (14:12), it should be carefully noted that  $h_m$ ,  $h_n$ ,  $h_o$ , and  $h_3$  are the specific enthalpies of the steam at the respective

points *in the turbine* and not at the position of these points as shown in Fig. 14:11; on that figure they would lie vertically below point 2. They are conveniently obtained from the Mollier diagram by continuing the same vertical projection from state 2 that was used to determine  $h_m$  to intersect the pressures at successively later extraction points and the pressure at the turbine exhaust. *The extraction of steam for feedwater heating does not reduce the quality of the steam flowing through the turbine to the condenser, but merely its quantity.*

Having made these preliminary calculations, the efficiency of this three-heater cycle can be obtained by applying Eq. (2:15). The heat  $Q_s$  supplied *by the source* heats the liquid from  $m''$  to  $c$  and then evaporates it to state 2; the amount of this heat per pound of steam entering the turbine is  $h_2 - h_{m''}$  or  $h_2 - h_{f_m} - \frac{(P_u - P_m)v_{f_m}}{J}$ . The amount of heat  $Q_R$  rejected *to the refrigerator* is  $(1 - M_m - M_n - M_o)(h_3 - h_{f_3})$ , and the cycle efficiency is

$$\begin{aligned} \eta &= \frac{Q_s - Q_R}{Q_s} \\ &= \frac{h_2 - h_{f_m} - \frac{(P_u - P_m)v_{f_m}}{J} - (1 - M_m - M_n - M_o)(h_3 - h_{f_3})}{h_2 - h_{f_m} - \frac{(P_u - P_m)v_{f_m}}{J}} \end{aligned} \quad (14:13)$$

Although the calculations outlined in Eqs. (14:8) to (14:13) have here, for clarity, referred to the three-heater cycle of Figs. 14:10 and 14:11, the same general method of calculation will apply to a cycle with any number of heaters. The pump arrangement shown in Fig. 14:10 is only one of a number of plans that can be used; for example, by draining the condensate from each heater into the heater at next lower pressure and, eventually, into the condenser, the number of pumps can be reduced to one, and the weight of condensate passing through each heater is the same. Note that this change would lower the efficiency of the cycle slightly, since the mixing of the condensate with steam at lower temperature will introduce an additional irreversibility which is avoided in the cycle as discussed above.

The irreversibility in the cycle which has been used here has arisen from the difference between the temperature of the steam in the heaters and the temperature of the feedwater as it entered the heater; otherwise the cycle efficiency would have equalled that of the Carnot cycle. The selection of the best points at which to extract steam from the turbine is based on keeping the average differential of temperature in the heaters to a minimum. This can best be approximated by dividing the total temperature interval between the saturation temperatures corresponding to the supply pressure  $p_u$  and exhaust pressure  $p_l$  into equal temperature drops between



inlet and the first extraction point, between extraction points, and between the last extraction point and the turbine exhaust. Thus it will be observed that, in Fig. 14:11, the length of the verticals 2- $m$ ,  $m'$ - $n$ ,  $n'$ - $o$ , and  $o'$ -3 have been made equal. Note that the number of these successive drops is one greater than the number of heaters. Another factor to be considered before a final selection is made is the design of the turbine, since an extraction point may be located only between stages of that unit.

When water is the working fluid and the temperature of the exhaust steam is not far above atmospheric temperature, a secondary advantage is associated with the regenerative vapor cycle. For example, at 100°F the saturation pressure of water is less than 1 psia, and the specific volume of dry saturated steam is about 350 ft<sup>3</sup>/lb. This compares with a specific volume of saturated steam at a supply pressure of 600 psia, corresponding to a saturation temperature of about 486°F, of about 0.77 ft<sup>3</sup>/lb, and indicates what a tremendous increase of volume has taken place during expansion through the turbine, even when allowance is made for the lower quality of the steam at exhaust. The very great volumes of steam that must be handled near the exhaust end of the turbine add to the difficulties of design of its low-pressure stages and to the size and cost of the turbine. In the regenerative cycle, the weight of steam flow is less through the lower pressure stages; this may amount to relieving these stages of one-quarter or more of the steam flow that must be handled at entrance to the turbine, and the difficulty mentioned above finds a partial solution.

The reheat and the regenerative cycles are both typically applied when the turbine is the prime mover and when the difference between  $T_s$  and  $T_R$  is large. The advantages of both cycles may be secured by combining their essential features in a single cycle, called the reheat-regenerative cycle. The supply steam enters the high-pressure turbine of Fig. 14:6 and may pass one or more extraction points before the unextracted portion is removed and reheated. Additional extraction points are usually located in the low-pressure turbine.

*Example 14:4.* A three-heater regenerative vapor cycle supplies saturated steam to the turbine at 600 psia. The exhaust pressure is 1 psia. (a) Choose suitable extraction points, and determine the specific enthalpy of the steam at each of these points and at entrance to and exit from the turbine. (b) Neglecting the effect of pump work, find the specific enthalpy of the feedwater at exit from the feedwater pump and from each of the regenerative feedwater heaters. (c) Calculate the weight of steam extracted to each heater per pound of steam entering the turbine. (d) Calculate the efficiency of the cycle, and compare it with those of the equivalent Carnot and Rankine cycles of Examples 14:1 and 14:2A.

*Solution:*

(a) The saturation temperatures equivalent to steam pressures of 600 and 1 psia are, respectively, 486.21 and 101.74°F, the total temperature interval being approximately 382 deg. Dividing this interval by one more than the number of heaters,  $\frac{382}{4} = 95.5^\circ$ .

Subtracting 95.5 from 486.2, the temperature at the first extraction point should be about 391°F, corresponding to a saturation pressure of around 225 psia. This pressure will be selected, in the absence of information as to the design of the turbine, as the pressure at the first point at which steam is extracted from the turbine. Continuing the same procedure, the temperatures at the second and third extraction points are found to be about 295 and 200°F, corresponding to pressures of about 62 and 12 psia. The specific enthalpies are obtained by vertical projection on the Mollier chart from state 2 and are as follows:  $h_2 = 1203$ ;  $h_m = 1123$ ;  $h_n = 1030$ ;  $h_o = 930$ ;  $h_3 = 807$ .

(b) The enthalpies of the feedwater at exit from the pump and from each heater are:

$$\text{At exit from pump } (h_f \text{ at 1 psia}) = 69.7 = h_{f_3}$$

$$\text{At exit from heater } H_o \text{ } (h_f \text{ at 12 psia}) = 170.0 = h_{f_o}$$

$$\text{At exit from heater } H_n \text{ } (h_f \text{ at 62 psia}) = 264.3 = h_{f_n}$$

$$\text{At exit from heater } H_m \text{ } (h_f \text{ at 225 psia}) = 366.1 = h_{f_m}$$

(c) From Eqs. (14:9), (14:11), and (14:12),

$$M_m = \frac{366.1 - 264.3}{1123 - 264.3} = \frac{101.8}{858.7} = 0.119 \text{ lb}$$

$$M_n = \left( \frac{1123 - 366.1}{1123 - 264.3} \right) \left( \frac{264.3 - 170.0}{1030 - 170.0} \right) = (0.881)(0.110) = 0.097 \text{ lb}$$

$$M_o = \left( \frac{1123 - 366.1}{1123 - 264.3} \right) \left( \frac{1030 - 264.3}{1030 - 170.0} \right) \left( \frac{170.0 - 69.7}{930 - 69.7} \right) = (0.881)(0.891)(0.1163) \\ = 0.091 \text{ lb}$$

(d) Applying Eq. (14:13) to compute the cycle efficiency,

$$\frac{(P_u - P_m)v_{f_m}}{J} = \frac{144(600 - 225)(0.01852)}{778} = 1.3 \text{ Btu}$$

and

$$\eta = \frac{1203 - 366.1 - 1.3 - (1 - 0.119 - 0.097 - 0.091)(807 - 69.7)}{1203 - 366.1 - 1.3} = \frac{324}{835.6} \\ = 0.388$$

This represents a considerable step from the Rankine-cycle efficiency of 0.348 (Example 14:2A) toward the limiting Carnot-cycle efficiency of 0.407 (Example 14:1).

Checking, the net work of the cycle is  $Q_S - Q_R$ , or 324 Btu/lb, from the calculation for efficiency above. The gross work per pound of steam entering the turbine may be calculated as

$$\frac{W_e}{J} = 1(1203 - 1123) + (1 - M_m)(1123 - 1030) + (1 - M_m - M_n)(1030 - 930) \\ + (1 - M_m - M_n - M_o)(930 - 807) \\ = 80 + (1 - 0.119)(93) + (1 - 0.119 - 0.097)(100) \\ + (1 - 0.119 - 0.097 - 0.091)(123) \\ = 80 + 82 + 78.4 + 85.3 = 325.7 \text{ Btu}$$

From this gross work must be subtracted the sum of the work of the pumps. The work of the feedwater pump is

$$\frac{(1 - M_m - M_n - M_o)(P_u - P_l)v_{f_l}}{J} = \frac{(0.693)(144)(600 - 1)(0.01614)}{778} = 1.2 \text{ Btu}$$

The work of condensate pump  $P_m$  below heater  $H_m$  is

$$\frac{M_m(P_u - P_m)v_{f_m}}{J} = \frac{(0.119)(144)(600 - 225)(0.01852)}{778} = 0.2 \text{ Btu}$$



The work of pump  $P_n$  is

$$\frac{M_n(P_u - P_n)v_{fn}}{J} = \frac{(0.097)(144)(600 - 62)(0.0174)}{778} = 0.2 \text{ Btu}$$

The work of pump  $P_o$  is

$$\frac{M_o(P_u - P_o)v_{fo}}{J} = \frac{(0.091)(144)(600 - 12)(0.01665)}{778} = \frac{0.2 \text{ Btu}}{1.8 \text{ Btu}}$$

The sum of the pump work is 1.8 Btu per pound of steam entering the turbine, and the net work of the cycle, calculated by subtracting pump work from the gross output of the turbine, is  $325.7 - 1.8 = 323.9$  Btu. This checks closely the value of 324 Btu obtained as the difference between  $Q_s$  and  $Q_R$ .

**14:5. The Ideal Vapor for the Heat Engine.** Water is the working fluid in the overwhelming majority of real heat engines that employ a vapor. But we have had occasion, in preceding pages, to point out a number of respects in which the characteristics of water are not those which we should prefer in the working fluid, and it is possible that some other vapor may be found which will better meet the requirements of a fluid for power generation. In order to systematize our search for this ideal vapor, let us set down the characteristics which it should possess.

1. It must be stable under all conditions through which it is to pass so that it will not dissociate.

2. It must not react chemically with the materials which, during various processes of the cycle, are called on to contain it.

3. It must not dissolve these materials with which it comes in contact in the course of the cycle.

4. It should be abundant in nature, cheap, and nonpoisonous.

5. Its critical temperature should exceed the metallurgical limit by a comfortable margin.

6. Its saturation pressure at the metallurgical limit should be moderate. Thus extremely high stresses in the walls of containers such as the boiler and superheater are avoided.

7. Its triple-point temperature should be below the temperature of the atmosphere (the temperature of the available refrigerator). Otherwise, condensation at atmospheric temperature might produce a solid, which would be difficult to transport through succeeding cycle processes.

8. Its vapor pressure at atmospheric temperature should not be too low. If below that of the atmosphere, noncondensable gases from the atmosphere may leak into the exhaust line between prime mover and condenser, and these must be pumped out of the condenser at considerable expense. Also, very low pressures mean very high specific volumes; it has been pointed out in the preceding article how large volumes add to the size and cost of equipment.

9. Its change of enthalpy during vaporization should be large as compared with the specific heat of the liquid. This causes the Rankine cycle

to conform more closely to the Carnot in its efficiency and makes unnecessary the expensive equipment required for regenerative feedwater heating.

10. Its entropy, as a saturated vapor at refrigerator temperature, should be only slightly greater than as a saturated vapor at the temperature at which it enters the prime mover. Taking into consideration the inevitable irreversibilities that accompany expansion in the prime mover, this would prevent either the accumulation of excessive liquid percentages in the exhaust or the rejection of some heat at a temperature above the available sink temperature which would accompany the constant-pressure cooling and condensation of superheated exhaust vapor. The effect of this characteristic would be to make it possible to supply the vapor to the turbine prime mover as a saturated, instead of a superheated, vapor and thus to take full advantage of the metallurgical limit; it would make unnecessary the expense of reheat-cycle equipment.

No one vapor satisfies all of the requirements listed above. Water fulfills specifications 1, 2, 3, 4, 7, and 9. With respect to items 8 and 10, its characteristics are fairly suitable, but it entirely fails to satisfy 5 and 6. Although a vapor which will improve on the characteristics of water over the entire range of temperatures between the metallurgical limit and atmospheric levels is not available, certain fluids have been suggested which have a more desirable behavior over more limited ranges of temperature and the possibility of using these in combination with water in a multivapor cycle has received considerable attention.

**14:6. The Mercury-Steam Binary-vapor Cycle.** Undoubtedly the most important of the fluids that have been suggested for use as a vapor for power generation, from the standpoint of the effort devoted to developing its use in a binary-vapor cycle with water as the other fluid, is mercury. Mercury has a critical temperature in excess of  $2800^{\circ}\text{F}$ , a triple-point temperature of  $-38^{\circ}\text{F}$ , and, at  $1000^{\circ}\text{F}$ , its saturation pressure is about 180 psia. It satisfies specifications 1, 2, 3, 5, 6, and 7 of Art. 14:5 quite adequately, and its characteristics are fairly satisfactory with respect to 9 and 10. It is not abundant in nature or cheap and, as a vapor, can be highly poisonous. Moreover, it entirely fails to meet the requirements of item 8, and this restricts its practical use to only the higher range of temperature since, at condenser temperatures approaching that of the atmosphere, it would be entirely impossible to hold the necessary condenser vacuum or to handle the tremendous volumes of mercury vapor that would be generated.

A number of power plants based on the use of mercury over the higher range of temperatures with steam as the fluid over the lower range have been developed and built by the General Electric Company. Some of these are now in semiexperimental operation, but equipment of this type



is not at present sold commercially because of considerations based on safety, dependability, and cost. The efficiencies realized have been encouraging, being as much as 20 per cent above those obtained in the operation of comparable plants using steam alone as the vapor.

A flow diagram for the mercury-steam binary-vapor power plant in its elementary form is shown in Fig. 14:12. Liquid mercury enters the mercury boiler and is evaporated to a saturated vapor. This evaporation may take place, as a limit, at the temperature fixed by the metallurgical limit of  $1000^{\circ}\text{F}$ , corresponding to a mercury-vapor pressure of 180 psia. After expansion to a suitable pressure of, say, 2 psia, corresponding to a

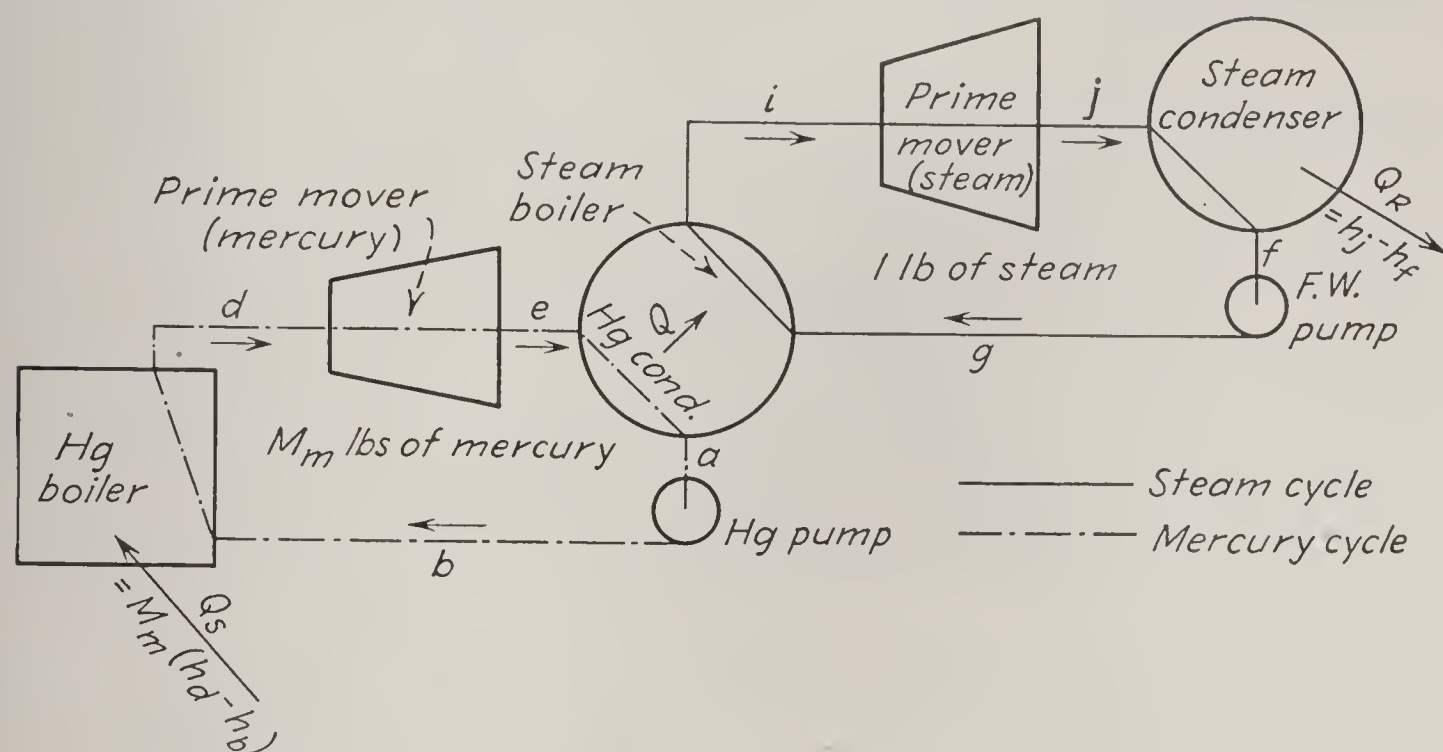


FIG. 14:12. Flow diagram—mercury-steam binary-vapor cycle.

temperature of about  $505^{\circ}\text{F}$ , in the mercury turbine, the exhaust mercury flows to a mercury condenser and is condensed. This mercury condenser is also a steam boiler, and, assuming a reasonable temperature differential between the mercury and steam to effect heat exchange between the two at the desired rate, steam evaporation could take place at a temperature of  $486^{\circ}\text{F}$ , corresponding to a steam pressure of about 600 psia. The mercury liquid, after leaving the condenser, passes through a pump which raises its pressure and forces it into the boiler, completing the cycle of the mercury.

The steam, leaving the steam boiler–mercury condenser unit, passes in turn through a steam turbine and steam condenser and is returned by a pump as feedwater to that unit; this constitutes a cycle of the water and steam entirely similar to cycles discussed earlier in this chapter, except as to the source of heat for evaporation in the boiler. If the steam is to leave the mercury condenser as a saturated vapor, the rates of flow of mercury and steam through their respective cycles must be proportioned so that the heat required to evaporate the feedwater into a saturated

vapor will be available from the heat given up by the mercury in condensing. Since mercury has much smaller enthalpies of vaporization than water, this requires that the flow of mercury be at a rate several times that of the flow of steam.

For purposes of clarity and an uncomplicated discussion, the binary-vapor power plant of Fig. 14:12 has been shown in its simplest form. Improvements in the efficiency of the plant and in practical features, such as the moisture percentage in the exhaust steam, could, for example, be

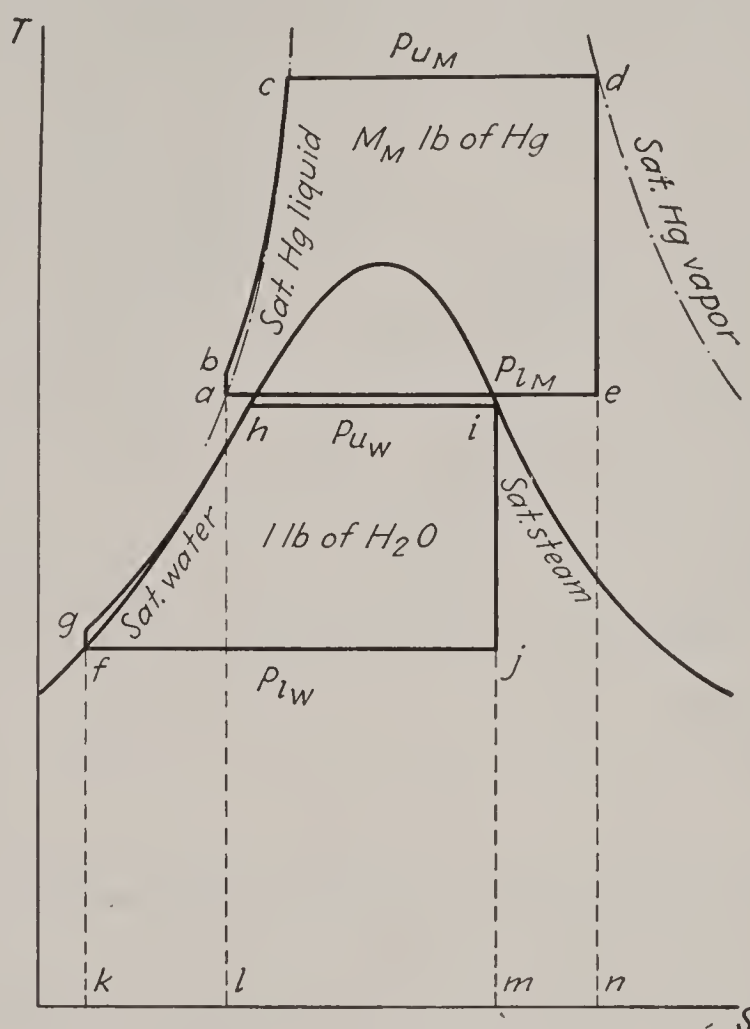


FIG. 14:13. Mercury-steam binary-vapor cycle.

made by allowing the saturated steam, after leaving the mercury condenser-steam boiler, to pick up further heat by bringing it into communication with the hot gases, produced as a result of the combustion of the fuel, as these gases leave the mercury boiler; or regenerative feedwater heating may be incorporated into the steam cycle, with a resultant improvement in the efficiency of that cycle and thus of the plant as a whole.

In Figure 14:13, the two cycles described above have been shown on the same temperature-entropy diagram. The cycle of the mercury is *abcde*, and that of the steam is *fghij*. The mercury-evaporation process *cd* is shown as extending between the saturated-mercury-liquid and saturated-mercury-vapor lines, but these lines are located not as for unit weight of mercury but with respect to a weight sufficient to cause the heat



rejected by the mercury in the mercury condenser-steam boiler (represented by area  $aenl$ ) to be equal to the heat absorbed by the unit weight of water and steam passing through the same unit (this heat is shown in the figure as area  $ghijmk$ ). Thus it is total entropies rather than the specific values of this property that are plotted in locating points  $a$  to  $e$ . The weight of mercury flow per pound of steam flow may be found by comparing  $h_e - h_a$  (for 1 lb of mercury) with  $h_i - h_g$  (for 1 lb of steam). This ratio of mercury flow to steam flow will be affected by introducing the practical factor of mercury-turbine efficiency and the effect of regenerative feedwater heating, if introduced into the steam cycle; the problem, in Fig. 14:13 and in the example to follow, has been reduced to its simplest proportions.

The efficiency of this binary-vapor cycle may be found by applying Eq. (2:15).  $Q_s$  includes only heat supplied by the source, or  $Q_s = M_M(h_d - h_b) = M_M \left[ h_d - h_a - \frac{(P_{u_M} - P_{l_M})v_a}{J} \right]$ , where  $M_M$  is the weight of mercury per pound of steam flow,  $h_a$  and  $v_a$  are, respectively, the specific enthalpy and specific volume of saturated-mercury liquid at the lower pressure  $p_{l_M}$  of the mercury cycle, and  $p_{u_M}$  is the upper pressure of that cycle. The heat rejected to the refrigerator is discharged during the condensation of the exhaust steam, and  $Q_R = h_j - h_f$ . The efficiency of the cycle is therefore

$$\eta = \frac{Q_s - Q_R}{Q_s} = \frac{M_M \left[ h_d - h_a - \frac{(P_{u_M} - P_{l_M})v_a}{J} \right] - (h_j - h_f)}{M_M \left[ h_d - h_a - \frac{(P_{u_M} - P_{l_M})v_a}{J} \right]} \quad (14:14)$$

The weight of mercury flow per pound of steam flow may be calculated as

$$M_M = \frac{h_i - h_g}{h_e - h_a} = \frac{h_i - h_f - \frac{(P_{u_w} - P_{l_w})v_f}{J}}{h_e - h_a} \quad (14:15)$$

in which  $P_{u_w}$  and  $P_{l_w}$  refer, respectively, to the upper and lower pressures of the steam cycle.

**Example 14:6.** In a binary-vapor cycle, mercury is supplied the mercury turbine as a saturated vapor at 180 psia. The mercury turbine exhausts to the mercury condenser-steam boiler unit at a pressure of 2 psia. The steam leaves this unit dry and saturated at 600 psia and is expanded in the steam turbine to a steam-condenser pressure of 1 psia. Find (a) the weight of mercury circulated per pound of steam flowing around its cycle and (b) the efficiency of the binary-vapor cycle.

*Solution:*

(a) The notation used in this solution will be that of Fig. 14:13. A table giving the properties of mercury vapor will be found in the Appendix. Reading from that table,

$h_d(h_g \text{ at } 180 \text{ psia}) = 151.1 \text{ Btu}$ ;  $h_a(h_f \text{ at } 2 \text{ psia}) = 17.65 \text{ Btu}$ ;  $h_{fg} \text{ at } 2 \text{ psia} = 125.8 \text{ Btu}$ ;  $s_e = s_d(s_g \text{ at } 180 \text{ psia}) = 0.1193$ ;  $s_a(s_f \text{ at } 2 \text{ psia}) = 0.02514$ ;  $s_{fg} \text{ at } 2 \text{ psia} = 0.1304$ .

Then

$$s_e = 0.1193 = s_a + x_e(s_{fg} \text{ at } 2 \text{ psia}) = 0.02514 + x_e(0.1304) \text{ or } x_e = 0.722$$

$$h_e = h_a + x_e(h_{fg} \text{ at } 2 \text{ psia}) = 17.65 + (0.722)(125.8) = 108.4 \text{ Btu}$$

In the cycle of the water and steam, points  $i$  and  $g$  correspond to points 2 and 1, respectively, of the cycle of Example 14:2A. In that example a calculation was made of the difference  $h_2 - h_1 = 1131.5 \text{ Btu} = h_i - h_g$ . Substituting in Eq. (14:15),

$$M_M = \frac{1131.5}{108.4 - 17.65} = 12.45 \text{ lb Hg per pound of H}_2\text{O}$$

Note that the irreversibilities encountered in the flow of mercury vapor through the real mercury turbine would have the effect of increasing  $h_e$  and thus of considerably reducing this ratio.

(b) The volume  $v_a$  of the liquid mercury is not shown in the table but, because of the high density of liquid mercury, is so small that the work of the mercury-liquid pump may be considered negligible. Applying Eq. (14:14),

$$\eta = \frac{12.45(151.1 - 17.65 - 0) - (807 - 69.7)}{12.45(151.1 - 17.65 - 0)} = 0.556$$

in which  $h_i$  and  $h_f$  correspond, respectively, to  $h_3$  and  $h_4$  of Example 14:2A and have been taken from the solution of that example. The efficiency of the equivalent Carnot cycle is  $\frac{999.6 - 101.74}{999.6 + 460} = 0.615$ .

### Problems

1. Sketch, on  $Ts$ ,  $hs$ , and  $pv$  coordinates, a Carnot reversible vapor cycle in which saturated steam is supplied at 400 psia to the prime mover which exhausts at 1 in. Hg abs. (a) What is its efficiency? (b) If the fluid enters the boiler as a liquid, what is its quality as it leaves the condenser? (c) What is the quality of the steam as it approaches the condenser? (d) How much heat is transferred, per pound of steam, in the boiler? (e) In the condenser? (f) On the basis of the answers to parts  $d$  and  $e$ , check your answer to part  $a$ . (g) What work is delivered per pound of steam by the prime mover? (h) How much work must be returned to drive the compressor? (i) What are the net work of the cycle and the work ratio? (j) What is the steam rate?

2. Describe the cycle of Prob. 1 as it might be carried out as a series of nonflow processes on a pound of  $\text{H}_2\text{O}$  confined in a cylinder closed by a piston. (a) What is the efficiency? (b) What is the work ratio? (c) What is the mep of the cycle?

3. Introduce into the cycle described in Prob. 1 the assumption that the engine efficiency of the prime mover and the adiabatic efficiency of the compressor are both 70 per cent. Answer the questions asked in Prob. 1.

4. What is the cycle efficiency in Prob. 1 if (a) the supply pressure is 200 psia? (b) If the exhaust pressure is atmospheric? (c) If both supply and exhaust pressures are changed as indicated?

5. In a Rankine cycle, steam is supplied to the prime mover at the same state and the exhaust pressure is the same as for the Carnot cycle of Prob. 1. (a) What is the quality of the steam as it approaches the condenser? (b) How much work is done per pound of steam by the prime mover? (c) How much work is required to



drive the feedwater pump? (d) What are the net work of the cycle and its work ratio? (e) How much heat is transferred, per pound of steam, in the steam generator? (f) In the condenser? (g) What is the efficiency of the cycle? (h) What is the steam rate? (i) Sketch the cycle on  $Ts$ ,  $hs$ , and  $pv$  coordinates. (j) Compare your answers with those of Prob. 1, and discuss.

6. Describe the cycle of Prob. 5 as it might be carried out in a cylinder closed by a piston as a series of nonflow processes. (a) What is its efficiency? (b) What is the work ratio? (c) What is the mep of the cycle?

7. Introduce the assumption that the prime mover and the feedwater pump each operates with an efficiency of 70 per cent into the cycle of Prob. 5. Answer the questions asked in Prob. 5.

8. What is the cycle efficiency if the following changes of data are made in Prob. 5? (a) The quality of the steam supplied the prime mover is 90 per cent. (b) The supply pressure is 200 psia. (c) The exhaust pressure is atmospheric. (d) Both supply and exhaust pressures are changed as indicated.

9. The cycle is the same as that of Prob. 5 except that the steam is superheated to 700°F before entering the prime mover. Answer the same questions asked in Prob. 5.

10. Assume that the efficiencies of prime mover and feedwater pump are each 70 per cent in Prob. 9. Answer the same questions.

11. Superheated steam is supplied the turbine prime mover at 400 psia. The exhaust pressure is 1 in. Hg abs. If the moisture percentage in the exhaust steam is not to exceed the maximum suggested in the text, to what temperature must the steam be superheated if the efficiency of the prime mover is (a) 70 per cent; (b) 75 per cent; (c) 80 per cent; (d) 85 per cent; (e) 100 per cent?

12. Superheated steam at 400 psia and 700°F is supplied to the high-pressure turbine of a reheat cycle and expands reversibly until its quality is 0.95. It is then extracted and reheated to 700°F before expanding reversibly in the low-pressure turbine to 1 in. Hg abs. (a) What is the pressure in the reheater? (b) What is the quality of the steam as it approaches the condenser? (c) Per pound of steam, how much work is performed in the high-pressure turbine? (d) In the low-pressure turbine? (e) What heat is transferred in the steam generator? (f) In the reheater? (g) In the condenser? (h) What is the cycle efficiency, and how does it compare with that of an equivalent Rankine cycle but without reheat? (i) Sketch the cycle on  $hs$  coordinates.

13. Steam is to be supplied the high-pressure turbine of a reheat-cycle plant at 1500 psia, superheated to 800°F. Condenser pressure is 1 in. Hg abs. Based upon reheating to 800°F, select a reheating pressure that will give equal and minimum percentages of moisture in the steam as it leaves the high- and the low-pressure turbines of the plant. What will that percentage of moisture be if (a) the expansions are reversible in both turbines and (b) if both have an efficiency of 85 per cent? (c) If both efficiencies are 80 per cent?

14. Work Example 14:4, changing the number of extraction points to two.

15. Work Example 14:4, changing the number of extraction points to one.

16. In Example 14:4, assume that the steam is superheated to 800°F before entering the turbine. Calculate the same quantities.

17. In a one-heater regenerative cycle, steam is supplied the turbine as saturated steam at 400 psia, and the condenser pressure is 1 in. Hg abs. (a) Select a suitable heater pressure. (b) Calculate the efficiency of the cycle, and compare with the efficiencies of the equivalent Carnot and Rankine cycles as computed in Probs. 1 and 5.

18. In a theoretical regenerative vapor cycle, steam is supplied to a 14-stage turbine at 500 psia and 640°F. The condenser pressure is 1 in. Hg abs. Assuming that the expansion in the turbine is isentropic and that equal work is performed in each stage, what are the pressures at the end of each stage? Select extraction pressures for (a) a four-heater cycle, (b) a three-heater cycle, to conform to the design of the turbine.

19. In a two-heater regenerative cycle, steam is supplied the turbine at 400 psia, 700°F. Condenser pressure is 1 in. Hg abs. If the extraction pressures are 100 and 12 psia, calculate the efficiency and compare with the efficiency of the cycle of Prob. 9.

20. In a combination of the reheat and the regenerative cycles, steam is supplied to the high-pressure turbine at 1200 psia and 900°F. After isentropic expansion in that unit to a pressure of 90 psia, all of the steam is extracted; a part goes to a regenerative heater, and the balance is reheated at constant pressure to a temperature of 600°F. The reheated portion is then expanded in the low-pressure turbine to condenser pressure of 1 in. Hg abs. The condensate is returned to the boiler through the regenerative heater by suitable pumps. Draw a flow diagram of this cycle similar to Figs. 14:6 and 14:10 and a  $T$ 's diagram that combines the features of Figs. 14:7 and 14:11, lettering the diagrams to correspond with each other. Per pound of steam supplied the high-pressure turbine, calculate (a) the weight of steam going to the feedwater heater, (b) the weight of steam reheated, (c) the heat added in the steam generator, (d) the heat added in the reheater, (e) the total heat added in the cycle from the fuel, (f) the heat rejected in the condenser, and (g) the total work of the cycle. (h) What is the efficiency of the cycle? (i) What is its steam rate? Neglect pump work throughout.

21. With respect to the features listed in items 1 to 10 of Art. 14:5, discuss the suitability as a vapor for power generation of the following: (a) ammonia; (b) sulfur dioxide; (c) Freon 12; (d) carbon dioxide. Would any of these vapors have any advantage as one of the vapors in a multivapor power cycle? If so, over what range of temperatures would it find use? What advantages would it possess over steam in this range? What disadvantages *in this range*?

22. In Example 14:6, assume that the efficiency of the mercury prime mover is 75 per cent and that of the steam prime mover is 80 per cent. (a) What is the ratio of the mass rates of flow of mercury and steam if the states of the vapors at entrance to the turbines are the same as in the example? (b) What is the efficiency of the cycle? (c) What are the qualities of the steam and mercury as they enter their respective condensers?

23. In Example 14:6, assume that the metallurgical limit is 980°F and that the pressure in the mercury condenser is 1 psia. A differential of 15°F is maintained between the temperature of the condensing mercury and the evaporating steam. The steam condenser operates at 1 in. Hg abs. What are the upper pressures of the mercury and the steam cycles? Calculate the weight of mercury circulated per pound of steam and the efficiency of the binary-vapor cycle.

### Symbols

$c_p$	specific heat at constant pressure
$h$	specific enthalpy
$J$	proportionality factor
$M$	mass rate of flow
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow, per cycle or per unit time



$s$	specific entropy
$T$	absolute temperature
$v$	specific volume
$W$	rate of work delivery
$x$	quality of the vapor

*Greek Letters*

$\eta$	efficiency of the heat engine; thermal efficiency
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*Subscripts*

$e$	engine
$i$	intermediate
$l$	lower
$L$	liquid
$M$	of the mercury (in the binary-vapor cycle)
$p$	pump; also, at constant pressure
$R$	refrigerator
$S$	source
$u$	upper
$V$	vapor
$W$	steam (in binary-vapor cycle)

## CHAPTER 15

### REFRIGERATION

**15:1. Introduction.** Refrigeration is defined as the production and maintenance of a temperature below that of the surroundings within the boundaries of a limited space. To accomplish this effect requires that the heat must be *continuously* removed from the contents of the space (called the *cold body*) and deposited with the surroundings (termed the *hot body*). The refrigerating machine must therefore operate on a cycle as it receives heat at a lower and discharges it at a higher temperature; it is, in its scheme of operation, a heat pump in the sense in which the use of that term was introduced in Art. 4:9 in connection with reversed operation of the Carnot engine. Although the heat pump may operate as a refrigerating machine, we shall make a distinction in the use of the two terms that is based on the purposes served as a result of the operation of the two devices. The heat pump, we shall say, has the objective of moving the heat from a lower to a higher temperature level, and the rate of its operation is fixed by the rate at which heat is to be discharged at the upper temperature; the objective in the operation of the refrigerating machine is to maintain a lower temperature in the cold body, and it removes only enough heat from that body to accomplish this effect.

Any reversible engine may operate as a refrigerating machine. In operation as an engine, it receives heat at a temperature above that of the atmosphere and discharges it at a temperature which may approach that of the atmosphere as a lower limit. As a refrigerating machine, on the other hand, the surroundings, in practice, usually consist of the atmosphere, and the temperature range of operation lies below the temperature of the atmosphere; thus the metallurgical limit, which has received so much attention in preceding chapters in connection with power cycles, is not a factor in the refrigeration cycle.

In developing the discussion of the refrigeration cycle, it will be our policy to consider that the temperatures of both hot body and cold body are constant. The atmosphere, which usually constitutes the hot body, is vast in extent, and the addition of finite amounts of heat to it will not alter its temperature appreciably. The cold body, on the other hand, comprises only a limited space, and we should ordinarily expect that the continuous removal of heat quantities from it would, ultimately at least, lower its temperature. But this cold body is immersed in higher tempera-



ture surroundings and simultaneously receives heat from these surroundings, as a result of the differential of temperature, as this heat is removed by the refrigerating machine; the maintenance of constant temperature in the cold space presumes that a delicate balance is maintained between the rate at which the refrigerating machine is operated and the rate at which heat leaks back into the space from the surroundings.

The rate at which it is capable of removing heat from the cold body is a measure of the *capacity* of the refrigerating machine, just as the capacity of the engine may be expressed in terms of its horsepower. The melting of ice is the traditional method of providing refrigeration, and it is not surprising to find that the recognized unit of capacity of the refrigerating machine is based on the refrigerating effect produced in terms of that melting. This unit of capacity is the *ton of refrigeration*, equivalent in refrigerating effect to that produced by the melting of 2000 lb of ice over a time period of 24 hr. Since the enthalpy of fusion of ice at atmospheric pressure is about 144 Btu, the rate of heat removal from the cold body which is defined as a ton of refrigeration amounts to 288,000 Btu in 24 hr, 12,000 Btu/hr, or 200 Btu/min.

Another distinction between the refrigeration cycle and the power cycle is found in the size of plant to which they are applied. The central-station power plant may be designed to meet the requirements of an entire area, such as a city or even a state, and large expense for equipment is often justified if its efficiency can be thereby increased in even small degree. On the other hand, the refrigerating machine is usually a much smaller device, and small savings that can be secured only by using complicated and expensive equipment are often ignored in favor of simplicity and lower first cost.

**15:2. The Reversed Carnot as a Refrigeration Cycle.** The Carnot engine cycle has been shown to be the power cycle of highest efficiency. As a reversible cycle when the temperatures of source and of sink are constant, it should offer possibilities as a refrigeration cycle which will be worth investigating.

In Fig. 15:1, the Carnot cycle has been plotted as a refrigeration cycle on  $T$ 's coordinates. It will be observed that the appearance of the cycle is unchanged from the form in which, in earlier chapters, we have so often had occasion to refer to it; however, the order of cycle processes is now different, and the limiting temperatures, denoted formerly by  $T_S$  and  $T_R$ , are now designated as  $T_H$  and  $T_C$ . Starting from state 1 of the figure, with the fluid at the temperature  $T_H$  of the hot body, the order of cycle processes is now as follows:

1. An isentropic expansion, 1-2, of the working fluid to the temperature  $T_C$  of the cold body.
2. An isothermal expansion, 2-3, at the temperature  $T_C$  of the cold

body during which the cold body gives up heat to the working fluid in the amount represented by the area 2-3-b-a of the figure; this may be designated as  $Q_C$  in the refrigerating cycle and is analogous to  $Q_R$  of the power cycle except in the direction of its flow.

3. An isentropic compression, 3-4, of the fluid to the temperature  $T_H$  of the hot body.

4. An isothermal compression, 4-1, at the temperature  $T_H$  of the hot body. During this process the hot body receives heat from the working fluid in the amount represented by the area 1-4-b-a, which may be designated as  $Q_H$  and is analogous to  $Q_S$  of the power cycle except in respect to its direction of flow.  $Q_H$  is obviously larger than  $Q_C$ , and since the isentropic processes take place without heat flow, their difference

must be equal to the net work which is *supplied* by external systems in the course of the cycle; this net work is represented by the area 1-2-3-4 enclosed within the cycle.

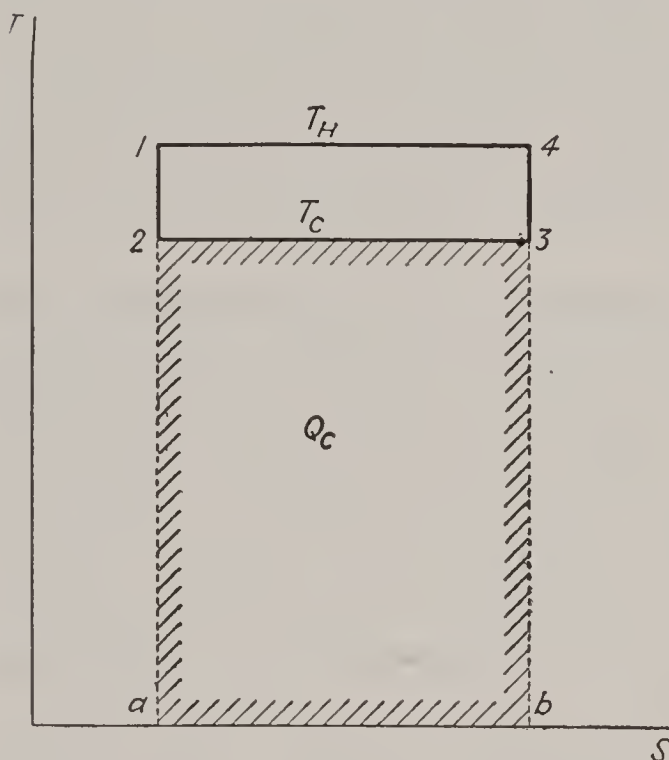


FIG. 15:1. The Carnot refrigeration cycle.

The cycle of Fig. 15:1 may, as we have seen, be traversed as a power cycle in a direction opposite to that described above; as a power cycle its efficiency is  $(T_H - T_C)/T_H$ . For a given hot-body temperature, this power-cycle efficiency could approach 1 as a limit as  $T_C$  approaches absolute zero, but in no case could it exceed that value, since negative

temperatures on any absolute scale of temperature have been shown to be an impossibility. As a refrigeration cycle, its effectiveness must be expressed on a somewhat different basis. The purpose of refrigeration is the removal of the heat quantity  $Q_C$  from the cold body; this is the useful effect that should be credited to the refrigerating machine in any attempt to rate its performance. The payment made to secure this useful effect is in the currency of work, the net work which must be furnished by external systems to carry out the cycle. The effectiveness of the Carnot refrigeration cycle is therefore expressible as the ratio of the area 2-3-b-a to area 1-4-3-2. It is noted at once that this ratio in Fig. 15:1 is greater than 1 and, in fact, could approach infinity as  $T_C$  approaches  $T_H$ . The ratio is not, therefore, to be classed as an efficiency; instead, the term *coefficient of performance* (cop) is used to express this ratio and thus to rate the performance of the Carnot refrigeration cycle and of all refrigerating



cycles and machines. Even a casual inspection of Fig. 15:1 will indicate that, since the  $Q_c$  and net-work areas are in proportion to their vertical heights, the coefficient of performance of the Carnot refrigeration cycle is  $T_c/(T_H - T_c)$ .

The principal value of the Carnot power cycle has been found in its proved status as a pattern cycle, *i.e.*, a cycle of maximum efficiency at given source and refrigerator temperatures. It would seem worth while to establish similarly the relative status of the Carnot refrigeration cycle; if it can be shown that associated with this cycle is the maximum coefficient of performance that is conceivable between given cold- and hot-body temperatures, the Carnot refrigeration cycle will become an important tool for the comparison of the performance of all refrigeration cycles and refrigerating machines with the ideal. To accomplish this purpose, let us assume, in a manner that is reminiscent of the method of proof of the Carnot principle in Chap. 5, that a refrigerating machine (working on a cycle and thus capable of continuous operation) is available which has a higher coefficient of performance than that of the Carnot when placed between cold and hot bodies at temperatures  $T_c$  and  $T_H$ , respectively. This would mean that, at the expenditure of the same amount of work that must be furnished by external systems to operate the Carnot refrigerating machine, a greater amount of heat  $Q_c$  could be removed from the cold body by this hypothetical machine and the heat  $Q_H$  delivered to the hot body would also be larger than in the operation of the Carnot machine. This heat  $Q_H$  could then furnish the heat supply to a Carnot engine, which would exhaust heat to the cold body. The work output of this Carnot engine would be greater than that required to drive the hypothetical machine, and since the hot body has given and received the same amount of heat and the only net heat exchange has therefore been with the cold body, a violation of the Second Law is evident. The assumption that a refrigerating machine may be devised that has a higher coefficient of performance than the Carnot when operating between the same limiting temperatures must therefore be abandoned. Thus the ideal, or maximum conceivable, coefficient of performance is that of the Carnot refrigeration cycle, or

$$\text{cop}_{\text{ideal}} = \frac{T_c}{T_H - T_c} \quad (15:1)$$

The coefficients of performance of refrigeration cycles and refrigerating machines will vary over a wide range according to the ratio  $T_c/T_H$ . The mere fact that a cycle or a machine shows a high cop is not an indication that no considerable improvement is possible; nor does a low cop necessarily mean that effort spent in an attempt to increase the performance will be rewarding, for this apparently low value may still be a

large fraction of the ideal cop if  $T_c$  is low in comparison with  $T_H$ . To express the ratio of the performance of the refrigerating cycle or machine to the ideal standard set by the Carnot refrigeration cycle, the term *refrigerating efficiency* is used. Efficiency in this case does not represent a ratio of output to input, as for the efficiency of a heat engine but, like the engine efficiency discussed in Chap. 13, is instead a ratio of actual to ideal performance. It may be expressed as the ratio of the actual cop to the ideal cop, or

$$\eta_r = \frac{\text{cop}}{\text{cop}_{\text{ideal}}} = \text{cop} \frac{T_H - T_c}{T_c} \quad (15:2)$$

The working substance in a refrigerating machine is called the *refrigerant*. When the refrigerant is a gas or a superheated vapor, the Carnot cycle suffers from the same or even greater handicaps as a refrigeration

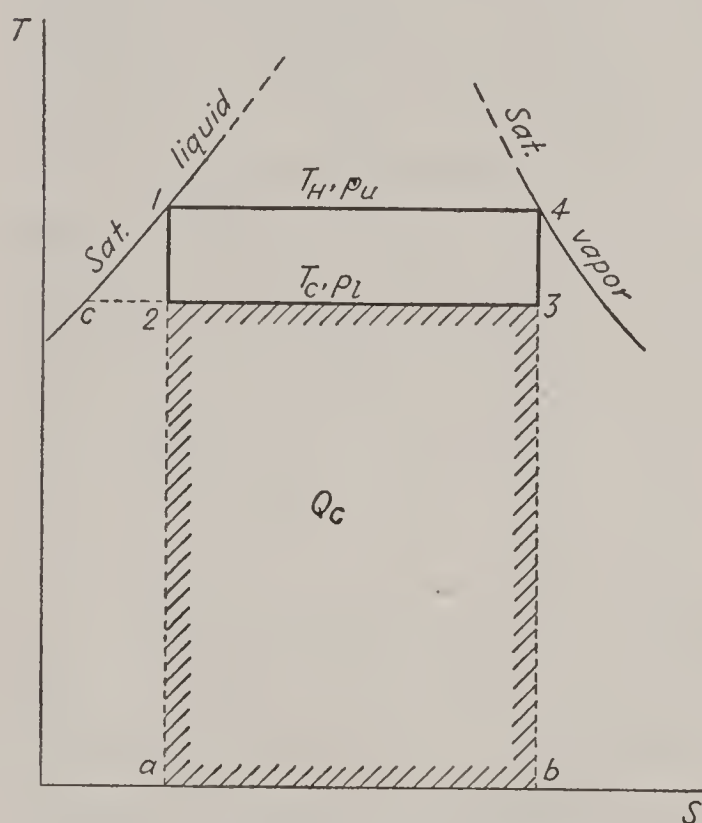


FIG. 15:2. The Carnot refrigeration cycle for a saturated vapor.

than as a power cycle, owing to the impracticability of heat transfer at constant temperature and the low work ratio of the cycle. For there was an advantage in using a gas as the working substance in the power cycle if internal combustion could thereby be employed and the temperature  $T_s$  increased above the metallurgical limit, while, in the refrigeration cycle, the range of temperatures falls, in practice, entirely below this limit. The use of a saturated vapor and a steady-flow cycle makes possible the transfer of heat simultaneously at constant temperature and at constant pressure, a practical method of steady-flow heat exchange. Moreover, the work ratio of the cycle is increased, and it is therefore considerably less vulnerable to the effects of friction and other irreversibilities in the real plant. Although air was formerly used as a refrigerant in some special situations, the vapor has now completely replaced the gas for the purpose.

In Fig. 15:2, the Carnot cycle of Fig. 15:1 has been placed between the saturated-liquid and saturated-vapor lines of a suitable refrigerant. The general description of the cycle is, however, the same as was outlined near the beginning of this article. The apparatus necessary for a demonstration of this cycle is shown in the form of a flow diagram in Fig. 15:3. The vapor engine accepts the saturated liquid at the upper pressure  $p_u$  and



upper temperature  $T_H$  of the cycle and expands it isentropically to the lower pressure  $p_l$  and lower temperature  $T_c$ . By applying Eq. (3:5), the work delivered by this unit may be shown to equal  $h_1 - h_2$ , per pound of refrigerant; this (positive) work is represented in Fig. 15:2 by the triangular area  $c-1-2$ . The refrigerant enters the evaporator as a wet vapor with a large percentage of moisture, as shown by the position of point 2 of Fig. 15:2. This evaporator is located in the cold room, so called because the purpose of operation of the machine is to maintain this space at low temperature. As the cold room receives heat from its surroundings, which are at higher temperature, it passes this heat on to the refrigerant as the

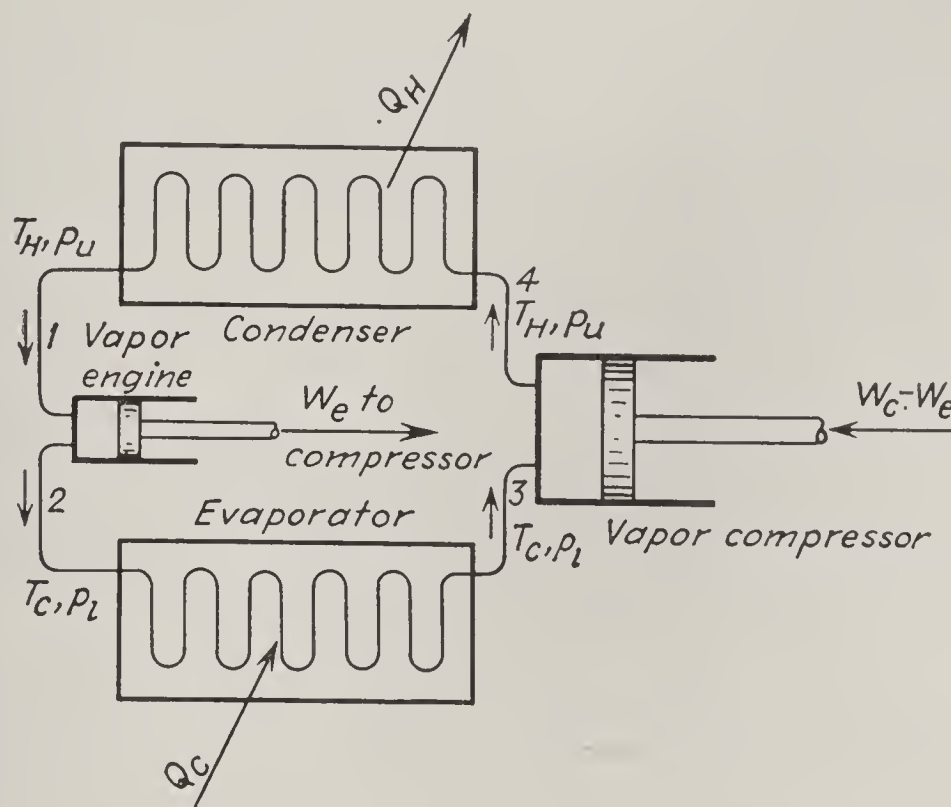


FIG. 15:3. Flow diagram—Carnot vapor-refrigeration cycle.

latter flows through the evaporator, with the result that the liquid gradually evaporates until the mixture leaves the evaporator at state 3 of Fig. 15:2. This represents the steady-flow transfer of heat in the amount  $h_3 - h_2$ , per pound of refrigerant, according to Eq. (3:5).

Entering the vapor compressor at state 3, the vapor is compressed isentropically to  $p_u$  and  $T_H$ . In Fig. 15:2, state 4 at exit from the compressor has been shown as a dry and saturated state, but both points 3 and 4 could move to the left (though not to the right) without affecting either the coefficient of performance of the cycle or the possibility of carrying out the steady-flow heat exchange in the condenser as a constant-pressure process. This is called *wet compression* since it is carried out entirely within the saturated-vapor region. The work of compression, from Eq. (3:5), is  $h_4 - h_3$ , per pound of refrigerant, and this work is represented by the trapezoidal area  $c-1-4-3$ . Taking into consideration the positive work of the engine, the net work of the cycle is represented by the rectangular area

1-2-3-4. The work ratio of the cycle is the ratio of this net-work area to the area  $c-1-4-3$ , and a comparison of these areas shows the work ratio to be high and therefore favorable. The last process of the cycle takes place in the condenser as the vapor is condensed to a saturated liquid at constant temperature  $T_H$  and constant pressure  $p_u$ . The heat rejected to the hot body in this steady-flow heat exchanger is  $h_4 - h_1$ , per pound condensed.

*Example 15:2.* A Carnot refrigeration cycle, using ammonia as the refrigerant, operates between a cold-room temperature of  $0^\circ\text{F}$  and atmospheric temperature of  $90^\circ\text{F}$ . (a) What is the cop of this cycle? (b) Calculate, based on the properties of ammonia, the heat removed from the cold body, the compressor work, engine work, and net work of the cycle per pound of ammonia flow. (c) Calculate, per ton of refrigeration, the mass flow rate, the volume of ammonia per minute handled by the compressor, and the power required. (d) What is the pressure ratio of compression?

*Solution.* The properties of ammonia may be taken from the abbreviated table that will be found in the Appendix.

$$(a) \text{ cop} = \frac{T_C}{T_H - T_C} = \frac{460}{90 - 0} = 5.11$$

$$(b) h_1 = h_f \text{ at } 90^\circ\text{F (180.6 psia)} = 143.5; s_1 = 0.2958$$

$$h_4 = h_g \text{ at } 90^\circ\text{F} = 632.0; s_4 = 1.1846$$

$$s_2 = s_1 = 0.2958 = s_{f_2} + x_2 s_{fg_2} = 0.0975 + x_2(1.2377) \text{ or } x_2 = 0.16$$

$$h_2 = h_{f_2} + x_2 h_{fg_2} = 42.9 + (0.16)(568.9) = 133.9 \text{ Btu}$$

$$s_3 = s_4 = 1.1846 = s_{f_3} + x_3 s_{fg_3} = 0.0975 + x_3(1.2377) \text{ or } x_3 = 0.878$$

$$h_3 = h_{f_3} + x_3 h_{fg_3} = 42.9 + (0.878)(568.9) = 542.5 \text{ Btu}$$

$$Q_C = h_3 - h_2 = 542.5 - 133.9 = 408.6 \text{ Btu/lb}$$

$$\frac{W_c}{J} = h_4 - h_3 = 632.0 - 542.5 = 89.5 \text{ Btu/lb}$$

$$\frac{W_e}{J} = h_1 - h_2 = 143.5 - 133.9 = 9.6 \text{ Btu/lb}$$

$$\text{Net work supplied} = 89.5 - 9.6 = 79.9 \text{ Btu/lb}$$

Checking,

$$\text{cop} = \frac{JQ_C}{W_{\text{net}}} = \frac{408.6}{79.9} = 5.11$$

This agrees with the answer to part *a*.

$$(c) M = \frac{200}{Q_C} = \frac{200}{408.6} = 0.49 \text{ lb NH}_3 \text{ per minute per ton}$$

$$V = Mv_3 = Mx_3v_{g_3} = (0.49)(0.878)(9.116) = 3.92 \text{ ft}^3/(\text{min})(\text{ton})$$

$$\text{hp} = \frac{(200)(778)}{\text{cop}(33,000)} = \frac{(200)(778)}{(5.11)(33,000)} = 0.92 \text{ hp/ton}$$

$$(d) \text{ Pressure ratio} = \frac{p_4}{p_3} = \frac{180.6}{30.42} = 5.93$$

**15:3. The Vapor-compression cycle** is a variant of the Carnot refrigeration cycle in which certain changes are introduced with the purpose of simplifying the apparatus needed for the refrigeration plant and making it easier to operate and maintain.



One change from the Carnot cycle which is always made in the real vapor-compression plant is the substitution of an expansion valve for the vapor engine of Fig. 15:3. Even if isentropic expansion in the engine were possible, the work delivered by this unit has been seen above to be relatively small. The irreversibilities which will always accompany its operation as a real device will still further reduce the amount of work delivery. The expansion valve is a simple device that amounts to a valve with an opening for the flow of refrigerant which can be enlarged or reduced in size according to the pressure on its downstream side. Thus the flow of refrigerant may be controlled automatically, increasing as the pressure in the evaporator falls and decreasing as this pressure rises.

The use of an expansion valve substitutes an irreversible adiabatic expansion for the reversible adiabatic process 1-2 of Fig. 15:2. This irreversible adiabatic process is of a throttling character and is similar to the process carried out in the throttling calorimeter and discussed in Art. 7:10. Thus  $h_2 = h_1$ , and state 2 moves horizontally to the right as indicated in Fig. 15:4. We should expect to find that the introduction of this irreversibility into the cycle has had the effect of lowering its coefficient of performance. This reduction in the coefficient of performance results both from the reduction in  $Q_c$  which accompanies the movement of state 2 to the right and from an increase in the net work of the cycle caused by the elimination of the work return formerly made by the vapor engine. The net work of the cycle is now the work of the vapor compressor, or  $h_4 - h_3$  per pound.

Another change from the Carnot refrigeration cycle that is usually found in the vapor-compression cycle consists in allowing the evaporation of the vapor in the cold room to continue until the vapor becomes dry; in Fig. 15:4, this alteration is shown in the shifting of point 3 to the right from  $e$ , which is its position in the Carnot cycle of Fig. 15:2. This causes state 4 at exit from the compressor to lie in the superheated-vapor region and is called *dry compression* to distinguish it from the wet-compression process of the Carnot cycle. Although it introduces a second irreversibility into the cycle and thus still further reduces the refrigerating efficiency, dry compression is usually preferred because of simplifications of

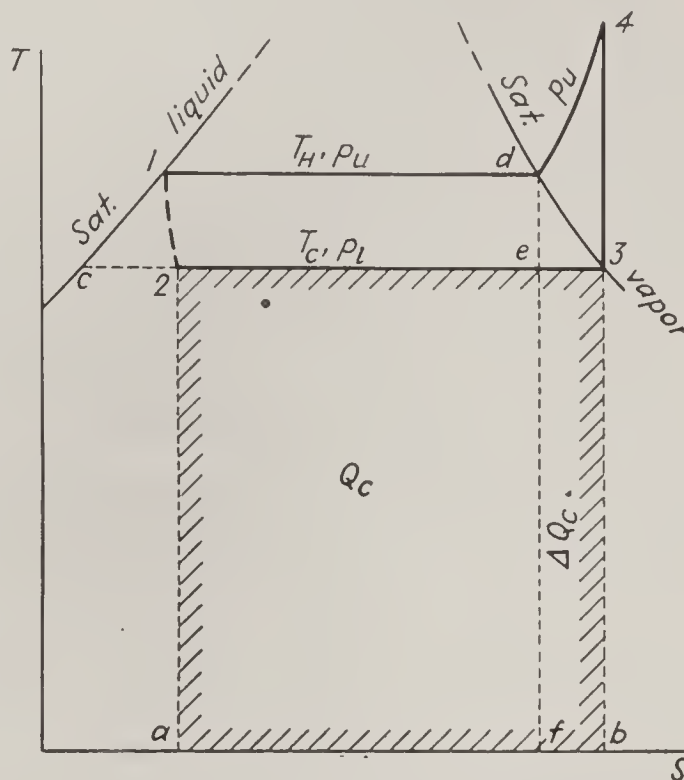


FIG. 15:4. The vapor-compression cycle—dry compression.

operation and control that are made possible in the real refrigerating machine. The vapor gives no readily observable signal as it approaches and passes point *e* of Fig. 15:4 in the course of its evaporation; neither its pressure nor its temperature undergoes any change along the entire path 2-3. Thus no indication is given either a human operator or an automatic-control apparatus that would aid in the operation of the compressor in such a manner or at such a rate that wet compression will be effected. On the other hand, if evaporation is allowed to continue to point 3 of Fig. 15:4, the passing of this point will be signaled by a rise in the temperature of the refrigerant as it begins to acquire superheat.

Dry compression has what appears to be a secondary practical advantage in that the  $Q_c$  area is increased as point 3 is shifted to the right (see area  $\Delta Q_c$  of Fig. 15:4), and thus the refrigerating effect is larger per pound of refrigerant circulated. This advantage is, however, less than it might appear, for the size of the compressor is determined by the *volume* of refrigerant it must handle and the specific volume at state 3 is greater than at state *e* of Fig. 15:4; also, heat exchange in both evaporator and condenser is greater per pound of refrigerant passing through those units, and their design must take this into consideration. Thermodynamically,  $\Delta Q_c$  is expensively obtained, for it requires the extra work area  $d-4-3-e$  of the figure. The coefficient of performance associated with the removal of  $\Delta Q_c$  from the cold body is therefore represented graphically in Fig. 15:4 as the ratio  $\frac{\text{area } e-3-b-f}{\text{area } d-4-3-e}$ . This ratio is less than the ideal cop of  $T_c/(T_H - T_c)$ , as is clear from a visual inspection of the proportions of the diagram, and it is evident that dry compression results in lowering the cop of the entire cycle. The irreversibility which is the thermodynamic explanation of this loss in performance consists in the “downhill” flow of heat during the desuperheating process 4-*d*; the coolant must be supplied at the temperature  $T_H$  or below if the later condensation  $d-1$  is to be possible.

In the real refrigeration plant, the temperature of the coolant must be somewhat less than the  $T_H$  of the cycle and the temperature of the cold room somewhat above that of the refrigerant in the evaporator if the heat exchange in the condenser and evaporator, respectively, is to proceed at the desired rate. These irreversibilities, combined with others encountered in the course of the circuit (principally in the compressor), cause the cop of the real plant to be less than that of the cycle on which its operation is based. The compressor of the real plant may be of either the positive-displacement or the centrifugal type, according to the volume of refrigerant it is required to handle and the differential of pressure,  $p_u - p_l$ .

The flow diagram of the vapor-compression cycle is presented in Fig. 15:5. The coefficient of performance of the cycle is



$$\text{cop} = \frac{JQ_c}{W_c} = \frac{h_3 - h_2}{h_4 - h_3} = \frac{h_3 - h_1}{h_4 - h_3} = \frac{h_3 - h_{fu}}{h_4 - h_3} \quad (15:3)$$

in which  $h_1$  ( $= h_2$ ) is the enthalpy of the refrigerant as a saturated liquid at condenser pressure  $p_u$  and  $h_3$  and  $h_4$  are, respectively, the specific enthalpies of the refrigerant at the beginning and the end of the isentropic compression.<sup>1</sup>

*Example 15:3.* For a vapor-compression refrigerating cycle using ammonia and operating between a cold-room temperature of 0°F and an atmospheric temperature of 90°F, calculate the coefficient of performance, the refrigerating efficiency, the heat

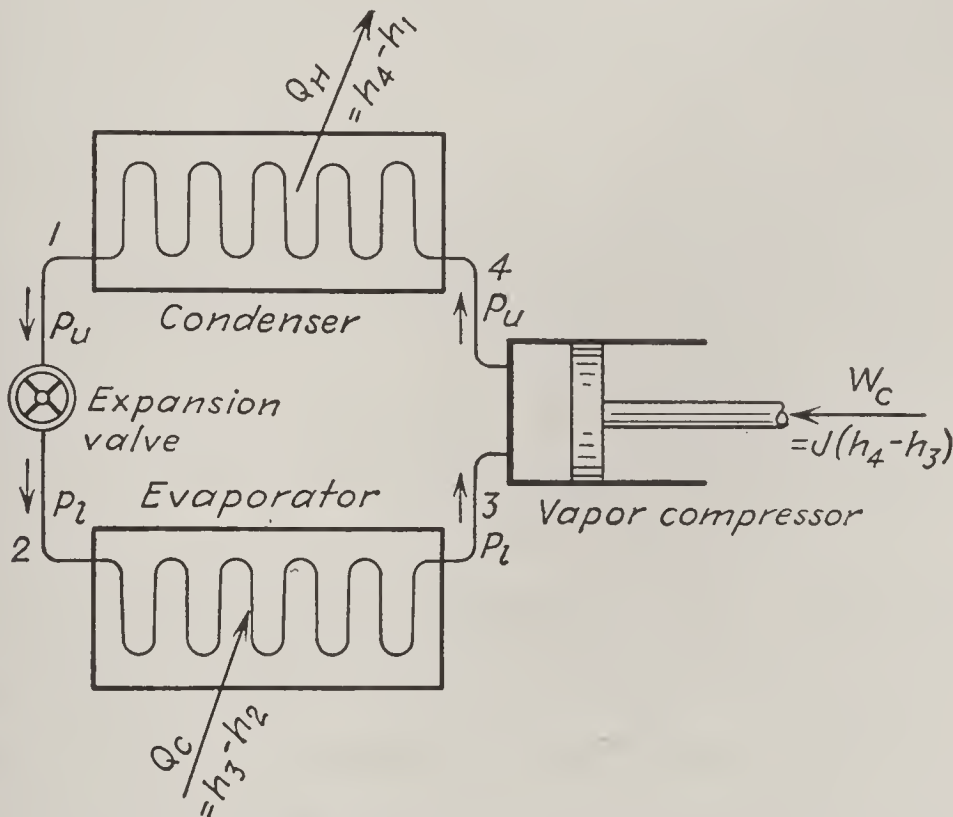


FIG. 15:5. Flow diagram—vapor-compression cycle.

removed from the cold body and the net work of the cycle per pound of refrigerant, and, per ton of refrigeration, the mass flow rate, the volume per minute handled by the compressor, and the horsepower required, for (a) wet compression, and (b) dry compression.

*Solution:*

(a)  $h_1 = 143.5$ ;  $h_3 = 542.5$ ;  $h_4 = 632.0$ ;  $x_3 = 0.878$  (see Example 15:2);  $h_2 = h_1 = 143.5$ . From Eq. (15:3),

$$\text{cop} = \frac{542.5 - 143.5}{632.0 - 542.5} = \frac{399.0}{89.5} = 4.46$$

$$\eta_r = \frac{4.46}{5.11} = 0.873$$

The substitution of an expansion valve for the vapor engine of the Carnot cycle accounts for this reduction of 12.7 per cent in performance.

<sup>1</sup> If wet compression is employed, point 3 shifts to position *e* of Fig. 15:4 and point 4 to *d*.

$$Q_C = h_3 - h_2 = 542.5 - 143.5 = 399.0 \text{ Btu/lb}$$

$$\text{Net work of cycle} = \frac{W_c}{J} = h_4 - h_3 = 632.0 - 542.5 = 89.5 \text{ Btu/lb}$$

$$M = \frac{200}{Q_C} = \frac{200}{399.0} = 0.501 \text{ lb/(min)(ton)}$$

$$V = M x_3 v_{g_3} = (0.501)(0.878)(9.116) = 4.01 \text{ ft}^3/\text{(min)(ton)}$$

$$\text{hp} = \frac{(200)(778)}{\text{cop}(33,000)} = \frac{(200)(778)}{(4.46)(33,000)} = 1.06 \text{ hp/ton}$$

(b) Use is made of the table of properties of superheated ammonia to find  $h_4$ :  $s_4 = s_3 = s_g$  at  $0^\circ\text{F} = 1.3352$ ;  $p_4 =$  saturated pressure at  $90^\circ\text{F} = 180.6 \text{ psia}$ . Interpolation in the table based on this pressure and entropy gives  $h_4 = 724.5$ .

$$h_3 = h_g \text{ at } 0^\circ\text{F} = 611.8; h_2 = h_1 = 143.5$$

$$\text{cop} = \frac{611.8 - 143.5}{724.5 - 611.8} = \frac{468.3}{112.7} = 4.16$$

$$\eta_r = \frac{4.16}{5.11} = 0.815$$

$$Q_C = h_3 - h_2 = 611.8 - 143.5 = 468.3 \text{ Btu/lb}$$

$$\text{Net work of cycle} = h_4 - h_3 = 724.5 - 611.8 = 112.7 \text{ Btu/lb}$$

$$M = \frac{200}{Q_C} = \frac{200}{468.3} = 0.427 \text{ lb/(min)(ton)}$$

$$V = M v_3 = (0.427)(9.116) = 3.90 \text{ ft}^3/\text{(min)(ton)}$$

$$\text{hp} = \frac{(200)(778)}{(4.16)(33,000)} = 1.13 \text{ hp/ton}$$

**15:4. Refrigerants.** Any refrigerant, if put through the succession of processes which we know as the Carnot refrigeration cycle, would yield the maximum coefficient of performance that is associated with that cycle. The choice of a refrigerant must therefore be made on the basis of how closely the processes of the real cycle, when applied to the refrigerant, may be made to approach those of the Carnot. Thus we have already had occasion to observe that the vapor has an overwhelming advantage over the gas if the cycle operations can be confined to handling the vapor in its saturated state. The choice of a suitable refrigerant consists of the selection of a vapor that will best meet the requirements.

In the real refrigeration cycle, the range of temperatures is between the upper limit fixed by the temperature of the atmosphere and a lower limit that is determined by the temperature which it is desired to maintain in the space to be cooled. This lower limit of temperature may be all the way from temperatures only slightly below that of the atmosphere down to temperatures as close to absolute zero as can be attained, and the selection of the vapor that is to be the refrigerant will depend upon the range of temperature through which its use is planned. When the over-all range of temperature is very large, it may be desirable, or even necessary, to apply the multivapor principle to refrigeration, in much the same manner as it has been applied in the mercury-steam binary-vapor cycle to the



power cycle. This is not done in ordinary commercial refrigeration, however.

Steam is preponderantly the vapor selected as the working fluid of the vapor power plant; in refrigeration a much wider selection of vapors is available, and resort may even be made to chemical synthesis, as in the case of the Freon series of refrigerants, to widen the field of selection. The desirable characteristics of the ideal refrigerant include:

1. It should be cheap, stable, nonexplosive, noncorrosive, and nonpoisonous and should not dissolve any of the materials which are used to confine it in the course of the cycle.

2. Its critical temperature should be well above the upper temperature of the refrigerating cycle so that condensation may take place, at least largely, at constant temperature.

3. Its saturation pressure at the upper temperature of the cycle should be moderate to prevent high stresses in the metal of the condenser and thus to reduce design difficulties and equipment costs.

4. Its enthalpy of vaporization should be large as compared with the specific heat of the liquid. The basis of this specification will be clarified when reference is made to Fig. 15:2. A low specific heat of the liquid would be reflected in greater steepness of the saturated-liquid line between *c* and 1 of that figure, and the work of the vapor engine of the Carnot cycle would be correspondingly less. When a shift is made to the expansion valve of the vapor-compression cycle of Fig. 15:4, the irreversibility of the latter cycle would be lessened and the movement of point 2 to the right of its position in the Carnot cycle would be shortened, resulting in a smaller reduction in  $Q_c$  as well as a smaller increase in the net work of the cycle. As a result, the refrigerating efficiency of the vapor-compression cycle is increased.

5. Its triple-point temperature should be well below the lowest temperature to be reached in the course of the cycle in order that there will be no chance of the formation of a solid.

6. Its saturation pressure at the lower temperature of the cycle should be slightly above atmospheric pressure. This provision both decreases the volumes that must be handled by the compressor and ensures that air will be prevented from leaking into the system.

7. The refrigerant, as a liquid, should wet the metal walls with which it comes in contact in the condenser and evaporator. This permits a reduction of temperature differential and of heat-transfer surface in these units by encouraging high rates of heat transfer.

8. Its entropy, as a saturated vapor, should be slightly less at the lower temperature of the cycle than at the higher. Allowing for the irreversibilities of the compressor, this would permit wet compression, even when

compression started from a dry saturated-vapor state such as point 3 of Fig. 15:4.

No refrigerant possesses all of the properties listed above. The particular refrigerant to be used is selected with a view to its suitability over the temperature range and under the conditions of operation that apply in the proposed plant. Water, the almost universally used fluid in the vapor power plant, is sometimes used as a refrigerant, but its use, because of grave shortcomings with respect to items 5 and 6, is confined to situations, as in air-conditioning installations, where evaporator temperatures below about 40°F are not required. Even at this temperature, tremendous volumes must be handled, and an ejector type of vapor pump is used as the compressor. Other, more commonly used refrigerants include ammonia, carbon dioxide, Freon 12, sulfur dioxide, methyl chloride, and propane. When the refrigerating efficiency of the cycle of Fig. 15:4 is calculated for these vapors over a typical temperature range, they all, with the exception of carbon dioxide, show a value of about 80 to 85 per cent. The refrigerating efficiency, when carbon dioxide is the vapor, is much lower, being less than 50 per cent, but carbon dioxide is none the less used to some extent on ships and in other situations where its nontoxic properties are of maximum importance; the Freon series of refrigerants are gradually replacing carbon dioxide, however, since they enjoy its advantages and, at the same time, make possible higher coefficients of performance. Ammonia is undoubtedly the most widely used refrigerant, the preference given it being based on items 2, 3, 4, 5, 6, and 7 above.

**15:5. Absorption refrigeration** is based on a cycle of the refrigerant very similar to that of Fig. 15:4 but substitutes a method of passing from state 3 to state 4 that does not require a vapor compressor. The change is made possible by the ability of some vapors to dissolve in certain solvents; in the commercial absorption-refrigeration plant the vapor is usually ammonia, and the solvent is water.

When anhydrous ammonia ( $\text{NH}_3$ ) is dissolved in water, a chemical change to  $\text{NH}_4\text{OH}$  takes place and heat is released as a result. The solution of ammonia in water is called *aqua ammonia*, and the concentration of ammonia in such solutions is expressed as a ratio of the weight of anhydrous ammonia which has been dissolved to the total weight of the solution; it is represented by the symbol  $x$ . When the concentration reaches a certain maximum, the water will refuse to accept any more ammonia in solution. This maximum concentration depends upon the pressure and the temperature of the solution, increasing with increased pressure and lowering as the result of higher solution temperature. When ammonia is dissolved in water at constant pressure, the heat release that accompanies the solution process will cause the solution temperature to rise, the point at which no more ammonia can be dissolved will soon be reached, and the



process will come to a halt. In order to make it possible for the solution to take place continuously, two steps must be taken: provision must be made for the continuous removal of heat from the solution so that its temperature will not rise above a permissible level, and some of the strong solution that is accumulating must be removed and replaced by fresh supplies of water or, at least, by aqua ammonia of lower concentration.

When it is desired to drive the ammonia out of solution at constant pressure, the temperature is raised to a level at which the aqua ammonia can no longer retain so large a proportion of ammonia in solution. To maintain this temperature as ammonia is driven off in a continuous process requires that heat be supplied continuously, since this chemical

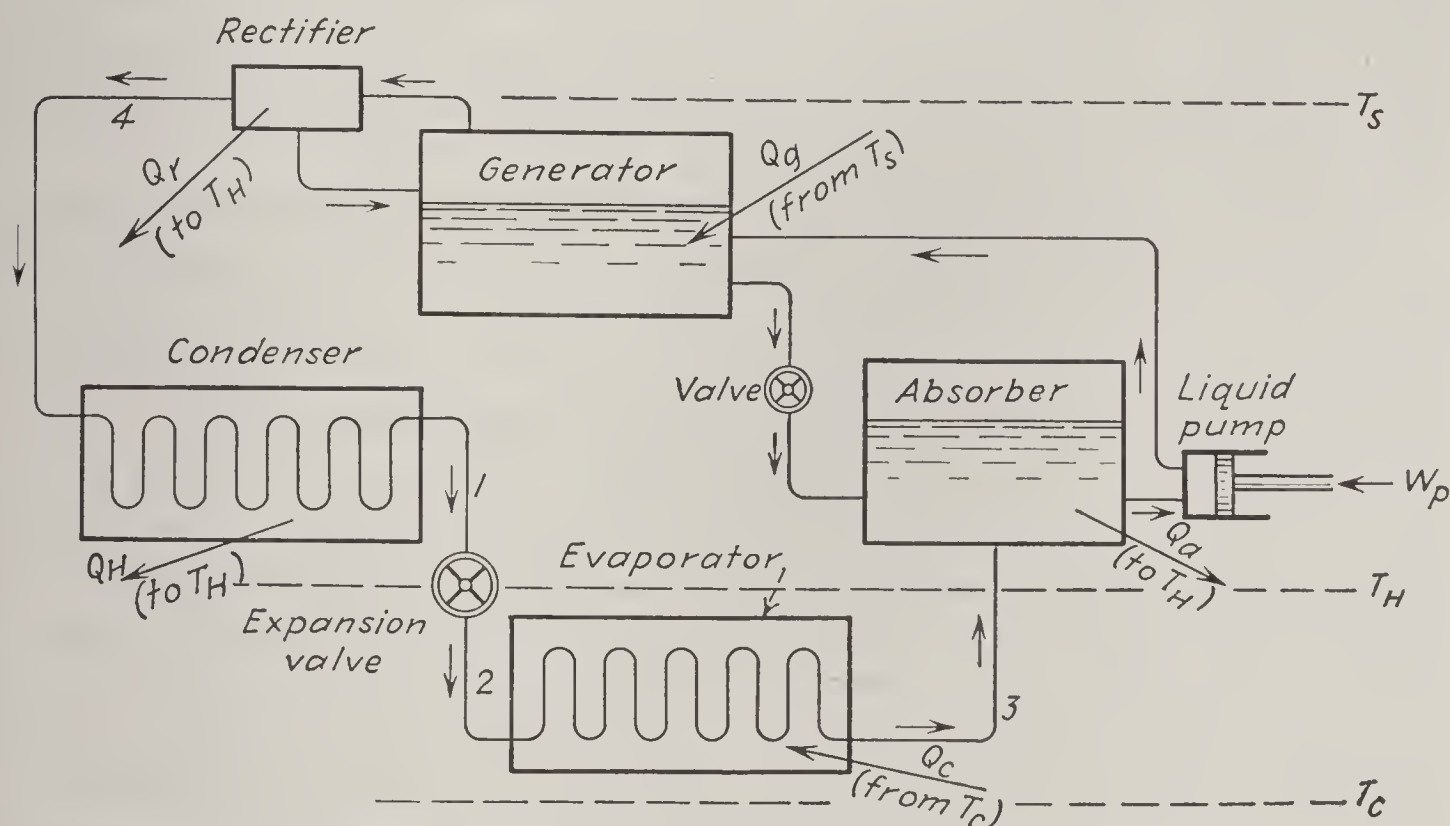


FIG. 15:6. Flow diagram—ammonia-absorption refrigeration cycle.

reduction of ammonia to the anhydrous form is endothermic, *i.e.*, requires the addition of heat from external systems if the temperature of the system is not to fall. As a result of the addition of this heat, certain amounts of water will also change to vapor form and escape into the space above the aqua ammonia, but the proportion of ammonia in the vapors above is much higher than in the liquid below. The small amount of water vapor in the vapor mixture can be largely reduced to liquid phase and returned to become again a part of the aqua ammonia if the vapors, after they have been transported to a location where they are no longer in communication with the aqua ammonia, are cooled to lower temperature.

The flow diagram of the ammonia-absorption refrigerating cycle is shown in Fig. 15:6. It will be observed that the apparatus concerned in the demonstration of processes 4-1, 1-2, and 2-3 remains the same as for the vapor-compression cycle of Fig. 15:5. In order to carry out process

3-4 of the vapor-compression cycle, equipment consisting of an absorber, a liquid pump, a generator or still, and a rectifier, or drier, replaces the vapor compressor of that cycle.

The dry anhydrous ammonia vapor leaving the evaporator at state 3 flows to the absorber, where it is allowed to bubble up through, and be absorbed in, the water contained in that unit. In order to make partial provision for continuous operation, heat is continuously removed from the aqua ammonia formed by this solution process at a rate sufficient to keep the temperature constant. This heat goes into cooling-water coils and thus is discharged ultimately to the atmosphere at the temperature level  $T_H$  of the vapor-compression cycle. The pressure in the absorber is approximately the same as that in the evaporator, since an open line connects the two. The temperature of the aqua ammonia in the absorber is only enough above  $T_H$  so that heat may be discharged at the required rate; this rate is designated as  $Q_a$  in the figure.

By cooling the aqua ammonia in the absorber, only partial provision has been made for continuous operation; in addition, aqua ammonia of high concentration must be removed and replaced by a weaker solution. Thus a liquid pump is provided which draws the solution from the absorber and discharges it into the generator. The pressure in the generator is the same as that of the ammonia in the condenser and thus is the higher pressure  $p_u$  of the vapor-compression cycle; the pump is therefore necessary to permit the passage of the liquid from absorber to generator against the differential between the pressures in the two units. It is in the generator that the ammonia is driven out of solution so that it alone can continue through the balance of the cycle. In order to do this, the temperature of the aqua ammonia must be raised, and heat must be continuously supplied. Since the temperature of the solution is already at or above that of the atmosphere, this heat  $Q_g$  must be supplied at some higher temperature, which we shall designate as  $T_s$ ; in the real ammonia-absorption plant, the temperature of the steam in the steam coils within the generator that furnish this heat is about 300°F. Because of the high temperature in the generator, the maximum concentration that can be maintained in the aqua ammonia which occupies the lower part of that unit is, in spite of the higher pressure in the generator, less than is maintained in the absorber, and ammonia vapor (with some water vapor) is driven out of solution and into the space above. The weaker solution that remains is drawn off and returned to the absorber, thus completing the requirements for continuous operation of both absorber and generator. No pump is necessary on this return line because the flow is in the direction of lower pressure, but a float-controlled valve ensures that the liquid levels in both generator and absorber will remain constant. The temperature of the liquid in this return line, to be later cooled in the absorber, is much higher



than that of the liquid in the line from absorber to generator, which is to be later heated in the generator, and the real absorption plant always uses a heat exchanger which brings the two lines into communication and allows the temperature of the liquid in the return line to be lowered and that in the other line to be raised. This is a feature which is not essential to the thermodynamic demonstration of the cycle and has been omitted from the figure to avoid possible confusion.

The ammonia vapor in the upper part of the generator is now ready to proceed through the balance of the cycle except that a small percentage of water vapor is mixed with it. To eliminate this water vapor, as far as possible, the vapor mixture is drawn out of the generator and passed through a rectifier, where it is brought into contact with cooling-water coils. The temperature of the mixture falls, as a result, and a large proportion of the water-vapor content is condensed and returned to the generator as a liquid. The rest of the vapor, now containing only a very small percentage of water vapor, continues its flow through the ammonia condenser, expansion valve, and evaporator to complete the cycle.

The advantage of the absorption over the vapor-compression system of refrigeration is found in the smaller amount of energy *in the form of work* that must be supplied by external systems to accomplish a given refrigerative effect. It has been shown previously that the work required for continuous compression may be measured as  $\int V dP$ , in which  $V$  is the volume of fluid compressed, or pumped, and  $dP$  is the differential of pressure. The differential of pressure is the same for both cycles, but the volume of vapor that must be handled by the vapor compressor in order to pass a unit weight of refrigerant around the cycle is very much greater than the volume of aqua ammonia handled by the pump of the absorption cycle in producing the same refrigerative effect. This is true in spite of the fact that the pump must handle a considerably greater *weight* of fluid than the compressor and results from the very small specific volumes of liquids in comparison with the specific volumes of their vapors. On the other hand, large amounts of energy *in the form of heat*, which must be supplied at a temperature well above that of the atmosphere, are required in the course of the absorption cycle, and this extra heat must ultimately be discharged to the atmosphere at the expense of the use of larger quantities of cooling water. The absorption plant is less flexible under variable-load conditions of operation and is more complex and expensive. The choice between the two systems should be based on the relative costs of energy in the form of heat and as work and upon the conditions of operation that are anticipated.

Equation (15:3) may not properly be used for the calculation of the coefficient of performance of the absorption refrigeration plant. The basic definition of the coefficient of performance of a refrigerating plant

or cycle is the ratio of the heat removed from the space to be cooled divided by the work which must be supplied by external systems to accomplish that refrigerative effect. If “work” in this definition is taken literally, the work of the liquid pump of the absorption cycle is so small that coefficients that are unreasonably high are obtained, values that would exceed the standard set by the Carnot refrigeration cycle by a wide margin. This basis of calculation would ignore the large amount of energy in the form of heat that must be supplied at a temperature above that of the atmosphere to carry out the absorption cycle. In the vapor-compression cycle, we are basically concerned with only two levels of temperature; these are  $T_c$ , the temperature of the cold room, and  $T_H$ , the temperature of the atmosphere. In the absorption cycle of Fig. 15:6, a third temperature  $T_s$  is added at which the heat  $Q_g$  is supplied at the generator. If this amount of heat had been furnished a Carnot engine which exhausted to the temperature of the atmosphere, an amount of work equal to  $Q_g(T_s - T_H)/T_s$  could have been made available. Constructively, if the negligible amount of work actually required to drive the liquid pump is ignored, this is the amount of work that should be charged to the operation of the absorption plant in calculating its coefficient of performance, or

$$\text{cop}_{\text{absorption cycle}} = \frac{Q_c T_s}{Q_g (T_s - T_H)} \quad (15:4)$$

When the coefficient of performance of the absorption plant is calculated on this basis, it cannot exceed the ideal set by the Carnot cycle and, in practice, will fall considerably below the cop of an equivalent vapor-compression plant.

Although the liquid pump of the ammonia-absorption cycle described above need be supplied work in only negligible quantities, it must be a positive-displacement device with moving parts because of the large differential of pressure between absorber and generator. The Electrolux refrigerator applies the principle of partial pressures to do away with this requirement. It was brought out in Chap. 10 that the temperature at which a liquid will evaporate into the space above will depend not upon the total pressure of all the gases that occupy that space but only on the partial pressure of its own vapor in the space.

If the temperature in the evaporator coils of the ammonia-absorption system is 0°F, the pressure of the saturated ammonia vapor is, according to tables of properties of ammonia, about 30 psia. In the condenser, an ammonia temperature of 90°F corresponds to a vapor pressure of about 180 psia; it is against a differential of pressure of this order that the liquid pump of the system would operate if ammonia alone were contained in the system. If, however, the pressure in the evaporator and absorber can be



built up to equal that in the generator and condenser by adding another gas in the evaporator and absorber in an amount sufficient so that its partial pressure will make up the difference between the ammonia-vapor pressures in the two parts of the system, a balance of *total* pressure around the circuit will be secured. The pump is concerned only with differences in total pressure and, in the case where that total pressure is balanced, need create only the small pressure differential necessary to overcome the frictional resistance to flow around the circuit at the desired rate. This frictional resistance is small if velocities are kept low and, in the Electrolux refrigerator, is overcome by allowing the aqua ammonia to enter the base of a vertical tube while heat is being supplied to it as it enters the generator. This heat causes the entering solution to release ammonia vapor, and the action is similar to the percolator of a coffeepot, the metal piston required in the mechanical pump being replaced by globules of vapor which force slugs of liquid ahead of them as they rise in the tube, thus overcoming the small total-pressure difference.

Hydrogen gas is used to build up the pressure in the evaporator and absorber of the Electrolux machine. The choice of hydrogen is based on its insolubility in water. It does not go into solution in the absorber and thus is not carried into the generator; a liquid seal is also used at the expansion valve to prevent it from backing up into the condenser, where its pressure would destroy the delicate balance of pressures that is required in the system.

The size of system to which the Electrolux principle may be applied is somewhat limited since a large system would offer resistances to flow too large to be handled by the percolator type of pump. In the past, its application has been limited to small household refrigerators, using a small gas flame to supply heat to the generator. More recently, its field of use has been widened to include the refrigerative air conditioning of buildings of limited size. In the latter application, it is of course necessary that the heat removed to the atmosphere from absorber and condenser be voided outside the space which is to be cooled.

**15:6. Adsorption refrigeration** is based on the property of some solids of attracting the vapor of a surrounding atmosphere and causing the formation of a dense layer of the vapor on the surface of the solid. The process of adsorption is accompanied by the release of heat, and the temperature of the adsorbing material will rise above the temperature of the atmosphere from which the vapor has been adsorbed. The maximum amount of vapor which may be adsorbed increases with decreased temperature and with increased pressure.

In a refrigerator that is based on the adsorptive principle, the solid is silica gel and the vapor sulfur dioxide. Two bodies of silica gel are provided; one is confined in a space at low pressure and adsorbs sulfur dioxide

at low temperature while the other, already charged with sulfur dioxide, is located in another compartment and gives off sulfur dioxide vapor as it receives heat. The vapor driven off in the high-pressure compartment passes through a condenser and is condensed; it then expands through an expansion valve into the low-pressure compartment and creates a low temperature in that space. The pressure in the low-pressure low-temperature compartment builds up only slowly because of the adsorption that is taking place in that space; in the meantime, refrigeration is provided by the evaporation of the liquid sulfur dioxide after it passes the expansion valve. Ultimately the process as described must come to a halt as the silica gel in the warm compartment gives up its sulfur dioxide content and that on the cold side of the expansion valve adsorbs it. The position of the two compartments is then reversed, that containing the silica gel which has been voided of sulfur dioxide being placed in the space to be refrigerated and the other heated so that the vapor held by its gel will be driven off. The pressure in the latter compartment builds up as the sulfur dioxide is driven off while, on the other side, the pressure drops as the gel begins to adsorb sulfur dioxide due to the lower temperature to which it is exposed. By means of a suitable valve arrangement, the condenser is placed on the opposite side of the expansion valve, and the direction of fluid flow is reversed. The commercial application of adsorption refrigeration is limited because of the intermittent character of its operation.

A schematic diagram of the flow which is described above is shown in Fig. 15:7. In the valve position shown, silica gel chamber  $C_1$  is being heated and the sulfur dioxide leaves  $C_1$  at high pressure and passes through the condenser and the expansion valve into  $C_2$ . In this second chamber, which is placed in the cold room, the silica gel is adsorbing the vapor. When the direction of flow is to be reversed, the valve is given a quarter turn clockwise and  $C_1$  is placed in the cold room while  $C_2$  is heated.

**15:7. Regeneration in Refrigeration—Liquefying Gases.** To liquefy any of the “permanent” gases requires that temperatures be produced that are far below the usual cold-room temperatures of the commercial refrigerating machine. For example, air at atmospheric pressure begins to liquefy at a temperature of about  $148^\circ\text{R}$ .<sup>1</sup> In utilizing the methods of refrigeration discussed to this point to produce a temperature of this order, a refrigerant must be selected which does not solidify at a higher

<sup>1</sup> The condensation of air, a mixture of gases, at constant pressure does not take place at constant temperature since the separate gases of which it is composed do not have the same saturation temperature at that pressure. The condensation of air at atmospheric pressure is not *completed* until a temperature of approximately  $142^\circ\text{R}$  is reached. During condensation the proportion of the constituents in the liquid changes, reaching the standard proportions for air only as condensation is complete.



temperature. Air itself would, of course, be a possibility, but, even at high pressures, the amount of reduction of temperature that can be obtained by throttling expansion through the expansion valve is limited and could not be expected to bring the temperature down from the atmospheric level in a single step. Adiabatic expansion behind the piston of an air engine would, in theory, increase the temperature drop, but, in practice, the irreversibilities that accompany such a process limit the temperature drop to less than the amount required.

Some temperature drop, based on its Joule-Thomson coefficient, can be obtained by throttling expansion of air, even at atmospheric levels of

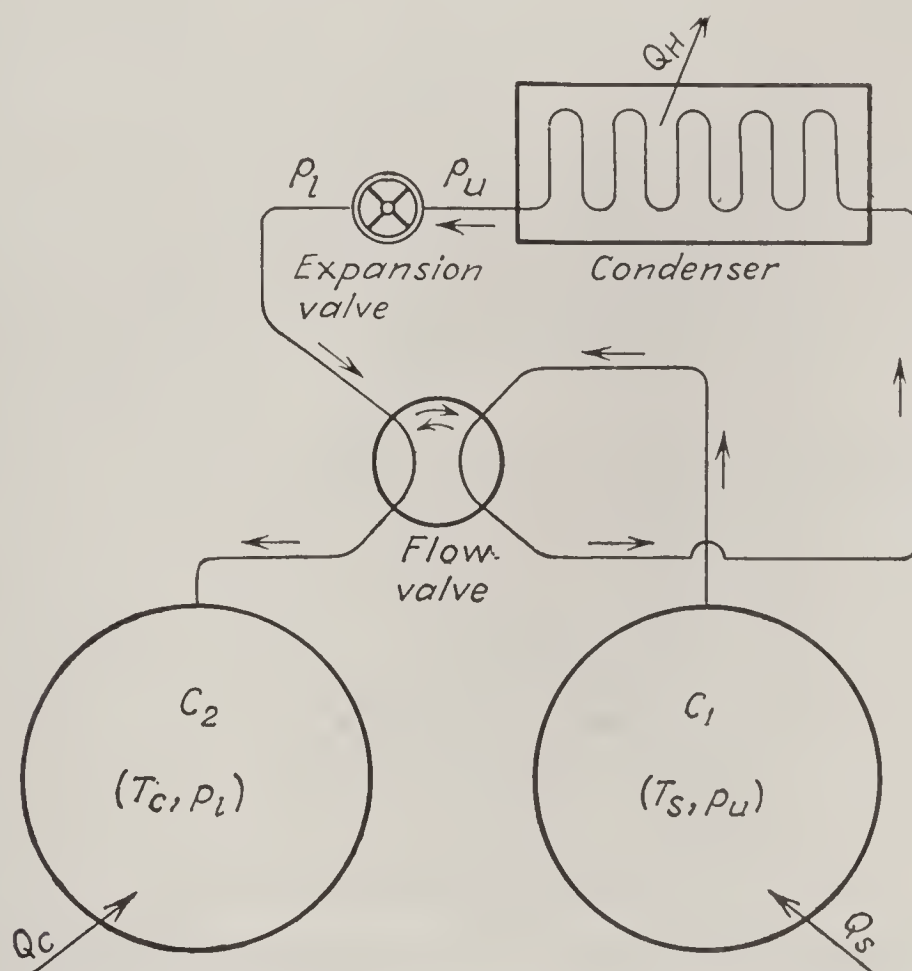


FIG. 15:7. Flow diagram for adsorption refrigeration.

temperature, and this drop is increased as the pressure from which the air is throttled is increased. The lower temperatures created in this manner can be used to chill the high-pressure air, before its expansion, to temperatures below that of the atmosphere, and so, after expansion, still lower temperatures may be created. This procedure can be continued until the temperature of the compressed air has been reduced to a really low level before its expansion, a level such that later throttling can produce a temperature low enough to result in partial condensation. This is *regenerative cooling* and is the basis of the Linde process for the liquefaction of gases.

The principle on which the Linde process is based is illustrated in the  $Ts$  diagram of Fig. 15:8 and the flow diagram of Fig. 15:9. Air at atmos-

pheric pressure and temperature is compressed in the compressor of Fig. 15:9 to a high pressure; this is process 1-2 of Fig. 15:8 and, as shown, causes a considerable rise in the temperature of the air. The next step is to cool the air to atmospheric temperature in the cooler shown in the flow diagram; this process is represented by the constant-pressure line 2-3 on the  $Ts$  diagram. Heat can be voided to the atmosphere only as low as atmospheric temperature, but constant-pressure cooling continues below  $T_3$  as the result of regenerative heat exchange with a stream of cool air, the source of which will be later explained. As a result of this regenera-

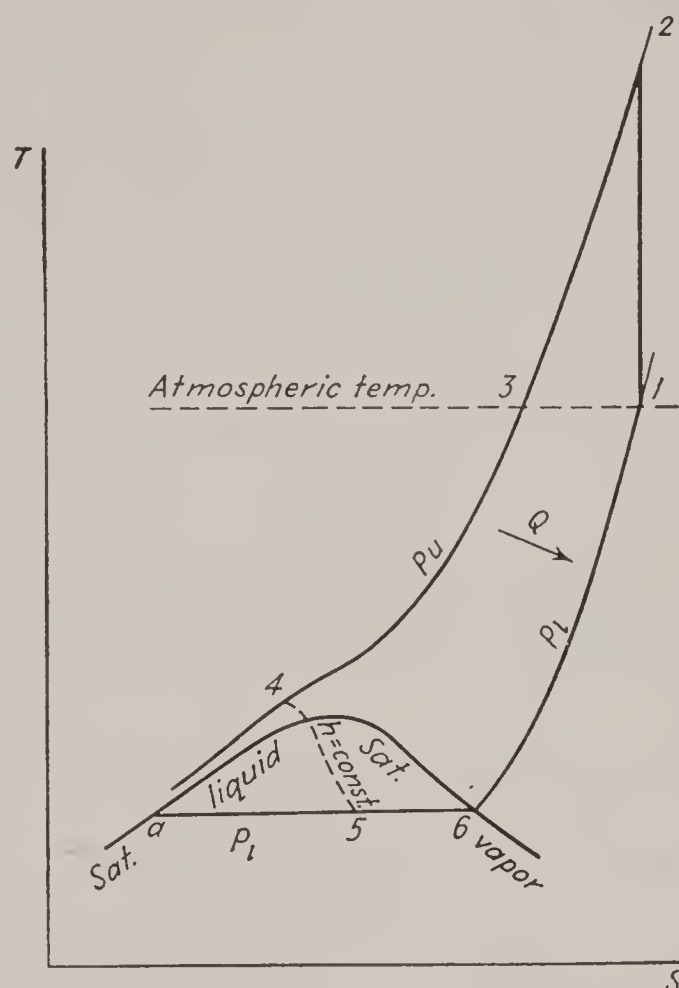


FIG. 15:8.  $Ts$  diagram—Linde process for liquefying air.

tive cooling, the high-pressure air is cooled to state 4. From this state it is possible, by throttling expansion to atmospheric pressure, to pass the fluid into its saturated-vapor region, as is shown in Fig. 15:8. As it issues from the expansion valve at state 5, the fluid is a mixture of the liquid and the dry vapor. On the  $Ts$  diagram, the weight of liquid per pound of mixture at this point is represented by the ratio  $\frac{\text{length of line 5-6}}{\text{length of line a-6}}$ . The greater density of the liquid makes it possible to separate it from the vapor and draw it off to storage. The rest of the mixture, a dry vapor, is brought into communication with the line carrying the air at high pressure in a counterflow heat exchanger and removes heat from the high-pressure air as the temperature of the vapor rises, ultimately to the temperature of the atmosphere. Now at atmospheric pressure and temperature, it may



reenter the compressor to retrace the process, although make-up must also be provided to replace the weight of liquid air which was withdrawn below the expansion valve.

In practice, the maximum differential of temperature that can be maintained by the method described above is about  $100^{\circ}\text{F}$ . The liquefaction of air directly from atmospheric temperature would therefore not be practical, but some vapor or vapors with suitable properties as refrigerants can be used to cover the gap in steps, or stages. This amounts to multivapor

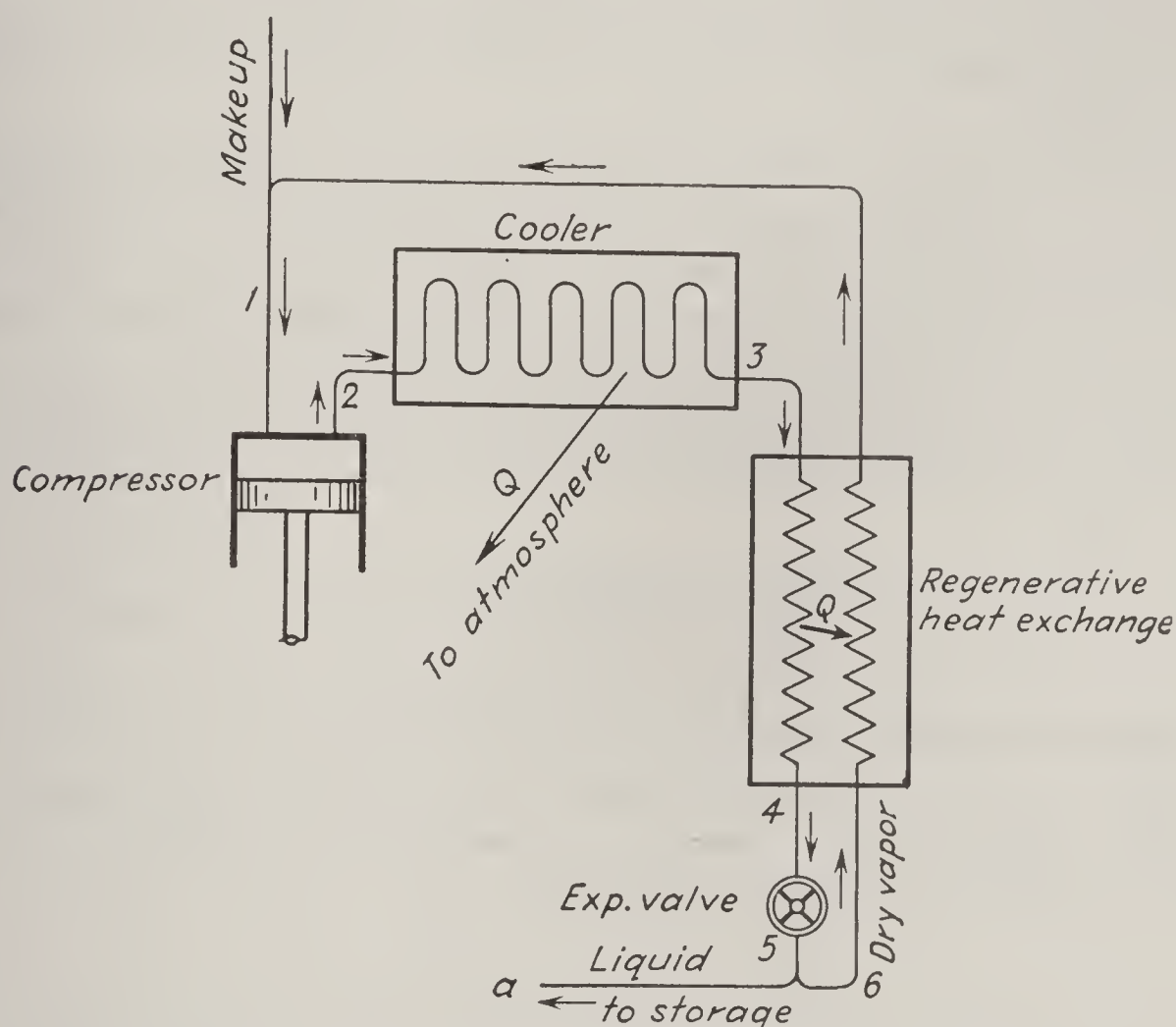


FIG. 15:9. Flow diagram—Linde process for liquefying air.

refrigeration and is analogous to the multivapor power cycle, as applied in the mercury-steam binary-vapor power plant.

Helium liquefies at about  $8^{\circ}\text{R}$  and requires the intermediate liquefaction of a number of vapors, hydrogen (liquefying at  $36^{\circ}\text{R}$ ) being the last preliminary step. By reducing the pressure acting on the liquid helium, temperatures of about  $1.5^{\circ}\text{R}$  may be attained; refrigeration based on the expansion of fluids cannot carry the temperature much below this level. The lower temperatures required in some scientific work are obtained by making use of the effect of extremely low temperatures on the magnetic properties of some substances. Temperatures below  $0.1^{\circ}\text{R}$  have been demonstrated by a method based on this phenomenon.

**15:8. The Heat Pump.** The heat required to maintain a comfortable temperature within buildings is ordinarily supplied directly from the

combustion of fuels. Work, in the form of electrical energy, may be used to accomplish the same purpose by passing the electric current through resistance heaters; but, as we have seen, work is a much more valuable form of energy than is heat, and this method, although sometimes used because of its convenience, is expensive. Moreover, it is thermodynamically wasteful, for a much smaller amount of work, if used to drive a heat pump, will account for the delivery of the required amount of heat. Space heating by this method, although still in the semiexperimental stage of development, has received considerable attention in late years, and there are many installations of the type in localities where conditions are favorable.

The heat pump is, in every respect except one, a refrigerating machine in principle. The difference lies in its purpose, which is to deliver heat at the higher temperature  $T_H$  instead of to remove heat from the colder body at  $T_C$ . This difference, however, requires a restatement of the coefficient of performance as it applies to the heat pump if the cop of the heat pump is to represent, as does the cop of the refrigerating machine, the ratio of the useful effect that is accomplished to the work required to produce that effect. Thus

$$\text{cop}_{\text{heat pump}} = \frac{JQ_H}{W_c} = \frac{JQ_C + W_c}{W_c} = \text{cop}_{\text{refrigerator}} + 1 \quad (15:5)$$

The ideal heat pump is based on the Carnot refrigeration cycle for which  $\frac{Q_H}{T_H} = \frac{Q_C}{T_C} = \frac{W_c}{J(T_H - T_C)}$ . The ideal, or maximum, coefficient of performance of the heat pump is therefore

$$\text{cop}_{\text{heat pump, ideal}} = \frac{T_H}{T_H - T_C} \quad (15:6)$$

The *heat-pump efficiency*, analogous to the efficiency of the refrigerating machine, rates the performance of the heat pump by comparing its cop with that of the ideal heat pump, or

$$\eta_{HP} = \frac{\text{cop}_{\text{heat pump}}}{\text{cop}_{\text{heat pump, ideal}}} = \text{cop}_{\text{heat pump}} \frac{(T_H - T_C)}{T_H} \quad (15:7)$$

The obvious low-temperature body from which heat may be “pumped” to the higher level of temperature to be maintained within the building is the surrounding atmosphere. Even in the milder climates, there is a wide variation between the extremes of temperature of the atmosphere during the heating season. The heat losses from the building, and thus the heat which must be supplied it at the higher temperature and the weight of fuel that must be burned in the conventional heating process to supply this heat, will vary approximately directly with the differential between



the temperature which is to be maintained within the heated space and that of the outside atmosphere. On the other hand, when the heat-pump method of heating is used, the cop of the heat pump will decrease as this spread of temperature widens and more work will be required to supply a given quantity of heat. This makes it evident that the best argument for the use of heat-pump methods in place of combustion heating will apply to its use in milder climates.

The variation of temperature of the earth, even at depths only a short distance below the surface, is much less than that of the atmosphere above, and the earth temperature, during the heating season, is higher than that of the atmosphere. This suggests that the water in wells, or even the earth itself, is a much more satisfactory source of the heat to be "lifted" to the temperature of delivery for heating purposes. A supply of water in the quantity required is often not available or is expensive to provide, and the design of heat exchangers capable of receiving heat directly from the earth is difficult, the performance of such exchangers varying greatly with soil conditions; these are the principal obstacles in the path of the commercial application of the heat-pump principle to the heating of buildings.

The use of the heat pump for the heating of buildings is, on the basis of present ratios of the cost of energy in the form of heat and as work, seldom economical from the standpoint of operational costs alone. The discrepancy in cost must be balanced by considerations based on greater cleanliness and convenience and by the fact that the heat pump may, by a suitable arrangement of valves, be operated on a refrigeration cycle during the season of summer heat and used to cool the building.

*Example 15:8.* A building has heat losses of 100,000 Btu/hr when the inside temperature is 70°F and the temperature of the air outside is 40°F. (a) Compare the cost of heating this building by burning oil and by using a heat pump which draws heat from the outside air, if the cost of oil is 6 cents per gallon, the calorific value of the oil is 137,000 Btu/gal, and combustion efficiency is 72 per cent and if the over-all heat-pump efficiency is 40 per cent and power costs 2 cents per kilowatthour. (b) Make the same comparison when the outside temperature is 10°F.

*Solution:*

(a) Combustion heater:

$$\text{Gallons of oil per hr} = \frac{100,000}{(0.72)(137,000)} = 1.015$$

$$\text{Cost of oil per hr} = (1.015)(6) = 6.1 \text{ cents per hour}$$

Heat pump:

$$\text{cop}_{HP} = 0.4 \frac{T_H}{T_H - T_C} = 0.4 \left( \frac{530}{70 - 40} \right) = 7.06$$

$$\begin{aligned} \text{Power to drive heat pump} &= \frac{100,000}{7.06} = 14,150 \text{ Btu/hr} = \frac{(14,150)(778)}{(1.34)(33,000)(60)} \\ &= 4.15 \text{ kw} \end{aligned}$$

Cost of power =  $(4.15)(2) = 8.3$  cents per hour

$$\text{Ratio } \frac{\text{cost of heat pump}}{\text{cost of oil}} = \frac{8.3}{6.1} = 1.36$$

(b) The differential of temperature is now doubled, and the heat losses will therefore increase to 200,000 Btu/hr. The cost of oil heating will also double to 12.2 cents per hour. For the heat pump:

$$\text{cop}_{HP} = 0.4 \left( \frac{530}{70 - 10} \right) = 3.53$$

$$\text{Power to drive heat pump} = \frac{200,000}{3.53} = 56,600 \text{ Btu/hr} = 16.6 \text{ kw}$$

Cost of power =  $(16.6)(2) = 33.2$  cents per hour

$$\text{Ratio } \frac{\text{cost of heat pump}}{\text{cost of oil}} = \frac{33.2}{12.2} = 2.72$$

The heat pump is in a relatively less favorable position than under the conditions of part *a*.

### Problems

1. Prove that all reversible refrigerating cycles must have the same coefficient of performance if they operate between the same hot- and cold-body temperatures.

2. A reversible refrigeration cycle removes heat from a cold body at a temperature of 10°F. The temperature of the atmosphere is 95°F. (a) What is its coefficient of performance? (b) What is its refrigerating efficiency? (c) If reversed and operated as a heat engine between the same temperatures, what would be its efficiency?

3. The temperature to be maintained in a refrigerator is 0°F. What is the ideal coefficient of performance if the temperature of the atmosphere is (a) 80°F; (b) 100°F?

4. The temperature of the atmosphere is 90°F. What is the ideal coefficient of performance if the temperature of the cold body is (a) 20°F; (b) 0°F?

5. A refrigerating machine removes heat from a cold room at 10°F and discharges it to the atmosphere at 100°F. Its refrigerating efficiency is 55 per cent. What power is required per ton of refrigeration?

6. A refrigerating machine with a refrigerating efficiency of 50 per cent discharges heat to the atmosphere at 90°F. Its coefficient of performance is 3.5. What is the temperature of the cold body? What horsepower is required per ton of refrigeration?

7. Assume that the plant diagramed in Fig. 15:3 is charged with a gas such as air, instead of a vapor. If used to remove heat from a cold room at  $T_C$  and discharge it to the atmosphere at  $T_H$ , what is the highest temperature that can be attained by the gas as it receives heat in passing through the cold room? What is the lowest temperature which the gas may reach as it delivers heat to the atmosphere? Assume that the compression and expansion processes are isentropic, and draw the cycle on  $Ts$  coordinates, comparing it with a Carnot cycle which operates between the same temperatures of cold room and atmosphere. In what sense is the gas cycle you have plotted a reversible cycle, and under what conditions is it not reversible? Discuss the relative advantages of a gas and a vapor as refrigerating mediums, based upon the  $Ts$  diagram.

8. In the gas refrigeration cycle that has been plotted on a  $Ts$  diagram in Prob. 7, assume the gas to be air, the temperature and pressure at the beginning of compression being 0°F and 30 psia. The temperature at the beginning of expansion is 90°F; the pressure is 70 psia. The heat-exchange processes are assumed to take place at constant pressure, and both compression and expansion are isentropic. (a) What is the



pressure of the air in the heat exchanger between compressor and engine? (b) Calculate the heat removed from the cold body, the compressor work, engine work, and the net work of the cycle per pound of air flow around the circuit. (c) Calculate the cop of the cycle, and compare with that computed in Example 15:2, when ammonia was used as the refrigerant. (d) Calculate, per ton of refrigeration, the mass flow rate, the volume of air per minute entering the compressor, and the net power required. Compare with the similar results in Example 15:2. (e) What is the refrigerating efficiency of the air cycle, based upon *constant* temperatures of cold room and atmosphere?

9. Work Example 15:2 using (a) sulfur dioxide, (b) F-12 Freon as the refrigerants. Compare with the results of the example, and discuss. From the standpoint of its ideal cop, which of the three vapors is the best? Could water vapor be used as the refrigerant under the conditions of the problem?

10. Discuss the effect of charging the plant that is diagramed in Fig. 15:5 with a perfect gas instead of a vapor. Show that in that case a temperature below that of the atmosphere could not be maintained in the cold room.

11. Work Example 15:3 for dry compression, using sulfur dioxide as the refrigerant. Compare with the results of the example, and discuss. From the standpoint of the cop of their cycles, which of the two vapors has the advantage under the conditions as stated? Contrast with the similar comparison that was made in Prob. 9. What difficulties would be encountered in the cycle if  $H_2O$  were used as the refrigerant?

12. Work Example 15:3 for wet compression, using (a) sulfur dioxide, (b) F-12 Freon as the refrigerants. Compare the coefficients of performance of the three refrigerants (include ammonia in the comparison) under the conditions of the example, and discuss.

13. Based on a cold-room temperature of  $40^\circ F$  and atmospheric temperature of  $80^\circ F$ , calculate the wet-compression coefficients of performance of the vapor-compression refrigeration cycle with (a) ammonia, (b) sulfur dioxide, (c) carbon dioxide, (d) F-12 Freon, and (e)  $H_2O$  as the refrigerants and compare. Compare the volumes that must be handled by the compressor per ton of refrigeration and the pressure range of compression.

14. Based on a cold-room temperature of  $40^\circ F$  and atmospheric temperature of  $80^\circ F$ , calculate the dry-compression coefficients of performance of the vapor-compression refrigerating cycle with (a) ammonia, (b) sulfur dioxide, and (c)  $H_2O$  as the refrigerants, and compare. Per ton of refrigeration, compare the volumes that must be handled by the compressor. What is the pressure range of compression in each case?

15. In Example 15:3, if the adiabatic efficiency of the compressor is 80 per cent in the dry-compression cycle, at what temperature does the ammonia leave the compressor? What is the coefficient of performance of the resulting cycle, assuming that points 1, 2, and 3 of the cycle are the same as in the example? What is its refrigerating efficiency?

16. Leaving the absorber of Fig. 15:6, the aqua ammonia has a temperature of  $80^\circ F$ , a pressure of 38 psia, a weight concentration  $x$  of 0.29, and a specific enthalpy of  $-40$  Btu/lb. Aqua ammonia is withdrawn from the generator at a temperature of  $305^\circ F$ , a pressure of 180.6 psia, a concentration of 0.13, and a specific enthalpy of 239 Btu/lb. Assuming complete rectification, (a) what weight of strong solution must the pump handle per pound of ammonia passing through the expansion valve? (b) What weight of weak solution is returned to the absorber from the generator? (c) What minimum work is required to drive the pump if the aqua ammonia is considered incompressible and to have a density of  $60$  lb/ft<sup>3</sup>?

17. (a) Based on the data and results of Prob. 16 and assuming that heat is not exchanged between the weak and the strong solutions and that the ammonia enters the absorber from the evaporator as a saturated vapor at  $10^{\circ}\text{F}$  with a specific enthalpy of 537 Btu/lb,<sup>1</sup> calculate the heat that must be removed from the absorber per pound of ammonia that passes through the expansion valve ( $Q_a$ ). (b) If a heat exchanger is employed and, per pound of ammonia passing through the expansion valve, 950 Btu of heat leaves the weak solution and enters the strong solution in the course of their flows between absorber and generator, what is the specific enthalpy of the weak solution as it enters the absorber and the specific enthalpy of the strong solution as it enters the generator? What is  $Q_a$  per pound of ammonia passing the expansion valve?

18. Continuing the study of the ammonia-absorption plant of Probs. 16 and 17 and making use of the data and results of those problems, assume that the vapors leaving the generator enter the rectifier at  $305^{\circ}\text{F}$ , 180.6 psia, and that the weight concentration of ammonia in these vapors is 0.60 and their specific enthalpy is 890 Btu per pound of mixture. Returning to the generator from the rectifier is aqua ammonia at  $305^{\circ}\text{F}$ , 180.6 psia, an ammonia weight concentration of 0.13, and a specific enthalpy of 239 Btu/lb. The pure ammonia leaving the rectifier and entering the condenser is a saturated vapor at  $90^{\circ}\text{F}$ . Per pound of ammonia passing from rectifier to condenser, find (a) the weight of vapor mixture entering and (b) the weight of aqua ammonia leaving the rectifier. (c) Calculate the heat ( $Q_g$ ) that must be supplied to the generator per pound of pure ammonia passing the expansion valve. Assume that the heat exchanger of Prob. 17, part b, is employed. (d) Calculate the heat that must be removed in the rectifier ( $Q_r$ ) per pound of ammonia passing the expansion valve. (e) Assuming that the pure ammonia enters the expansion valve as a saturated liquid, calculate  $Q_H$  and  $Q_C$  per pound of ammonia passing that valve. (f) Prepare an energy-balance for the entire plant, based on the First Law.

19. Calculate the coefficient of performance for the ammonia-absorption refrigeration plant of Probs. 16 to 19. What is the lowest temperature that may be substituted for  $T_S$ ? What is the highest temperature that may be used as  $T_H$ ? What is the refrigerating efficiency of the cycle?

20. Equation (15:4) is an approximation that ignores the work of the liquid pump of the absorption-refrigeration cycle. Based on including that work, what coefficient of performance would be obtained in Prob. 19?

21. A building has heat losses that total 150,000 Btu/hr when the inside temperature is  $70^{\circ}\text{F}$  and the outside temperature is  $30^{\circ}\text{F}$ . If a heat pump is used to heat the building and it has an efficiency of 45 per cent, what horsepower will be required when the temperatures are as specified above? What is the coefficient of performance of the heat pump? What are the similar answers if the outside temperature drops to  $20^{\circ}\text{F}$ ?

22. When the inside temperature is  $70^{\circ}\text{F}$  and the outside temperature is  $35^{\circ}\text{F}$ , a building has heat losses of 75,000 Btu/hr. The coefficient of performance of a heat pump which draws heat from the atmosphere and is used to heat this building is 6.5. When the temperatures are as specified above, what power is required? At what rate is heat removed from the atmosphere? What is the efficiency of the heat pump?

<sup>1</sup> This enthalpy may be obtained from the Bureau of Standards table of the properties of ammonia by subtracting 78 Btu from the values shown in that table. This is done in order that they will be based on the same reference level as the Jennings and Shannon tables, from which the enthalpy of the weak and the strong solutions has been taken.



## Symbols

$\text{cop}$	coefficient of performance
$h$	specific enthalpy
$J$	proportionality factor
$M$	mass rate of flow
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$Q$	rate of heat flow
$s$	specific entropy
$T$	absolute temperature
$v$	specific volume
$V$	volume; volume rate of flow
$W$	rate of work delivery
$x$	quality of the vapor; also, concentration of ammonia in aqua ammonia

*Greek Letters*

$\eta_r$	refrigerating efficiency
$\eta_{HP}$	efficiency of a heat pump

*Subscripts*

$a$	absorber
$c$	compressor
$C$	cold body
$e$	engine
$f$	of the saturated liquid
$g$	of the saturated vapor; also, generator of the absorption cycle
$H$	hot body
$HP$	heat pump
$l$	lower
$R$	refrigerator
$S$	source
$u$	upper

## CHAPTER 16

### THE EVALUATION OF IRREVERSIBILITY

**16:1. Introduction.** A heat engine operates on a cycle with the purpose of accomplishing a continuous conversion of energy from the form of heat into the form of work. Its effectiveness in fulfilling that purpose is measured in terms of the ratio of the rate at which work is delivered to that at which heat is received; no heat engine can convert all of the heat that it receives into work. Its performance is rated by comparing it with that of the ideal reversible heat engine which receives heat under the same conditions and exhausts it to the same reservoir (refrigerator, or sink), and this reservoir is characteristically represented, for the engineer, by the atmosphere. Any failure to attain the ideal performance associated with this reversible engine can be attributed to irreversibilities that have been encountered in carrying out one or more of the processes of the heat-engine cycle. These processes are ordinarily carried out in the real power plant in separate devices, each responsible for the demonstration of a part of the entire cycle. In order to improve the performance of the entire heat engine, by reducing its irreversibility, it is desirable that each of the processes making up the cycle be individually studied for its irreversibilities; in that way, the source, or sources, of the trouble may be located and may receive proper attention. Any other method may be misleading. For example, the steam, as it enters the condenser of the steam power plant, contains large amounts of energy which are immediately discarded to the atmosphere; this is sometimes listed as the "exhaust loss" in analyzing the performance of the engine. But even the ideal Carnot engine has a large "exhaust loss," which is based on the standards set by the Second Law, and attention given to reducing this "loss" will be rewarding only if it is larger than is warranted under the conditions that surround the operation of the engine and if the source of the irreversibility which accounts for the excess is known.

A similar discussion will apply to the execution of a cycle which has for its purpose the maintenance of a temperature below that of the atmosphere within a limited space, as by a refrigerating machine, or the delivery of heat taken from the atmosphere to a body at higher temperature, the purpose of the heat pump. The performance of plants of this kind can be improved only within the limits of performance set by the ideal (reversible) refrigeration cycle, and this improvement is possible only as the



irreversibilities encountered in the individual processes of the cycle are reduced. Unless and until the magnitude of the irreversibility encountered in each individual process of the real cycle is calculated and considered as to its effect on the performance of the entire machine, effort may not be intelligently directed toward improvement of that performance.

**16:2. Availability.** A system, as it enters a process at a state which will be designated by the subscript 1, possesses a store of energy dependent on its pressure, its temperature, its position, its motion, and its electricity and magnetism. In combination with a vast *medium*, or atmosphere, having the pressure  $P_0$  and the temperature  $T_0$ , it will be capable of delivering a portion of this store of energy in the form of work to external systems other than the medium as it shifts to a *dead state*, at which it is at rest within the medium and is in equilibrium with it as regards pressure, temperature, and electricity and magnetism. On the other hand, if it is already at the dead state, no work may be obtained from the system or from the medium either individually or as the result of interaction between the two.<sup>1</sup>

If the system is not at its dead state, a tendency will exist for a change toward the dead state. In order to initiate this change of state, it may be necessary for some external system (other than the medium) to furnish the necessary disturbance, but, once started, a portion of the work released as a result of the change of state may be used to restore to this external system the energy that has been borrowed from it, and, because of the spontaneous character of the change, it will always be possible to deliver an excess of (positive) work to the surroundings. This will be true even if, originally, the temperature and/or the pressure are below those of the medium. For if the temperature of the system is originally less than that of the medium, heat may be supplied by the medium to a Carnot engine which has the system as its sink and work will be obtained while the temperature of the system, as it receives heat from the exhaust of this Carnot engine, gradually rises toward the dead-state temperature; simi-

<sup>1</sup> It is assumed that there is no relative movement between parts of the medium, nor does any difference in pressure (at the same level), temperature, or composition exist throughout its extent; otherwise, the medium alone would always constitute a source of work. When, in the course of a process, the system combines, either chemically or mechanically, with a portion of the medium, as in the combustion of a fuel, that portion is made a part of the system, the latter being described to include it throughout the entire process. Thus, in the combustion process, the system is described to include, at the beginning of the process, the fuel plus that portion of the atmosphere which will ultimately enter into the process. The medium does not include this portion, which, in the course of the process, may change in temperature or pressure; the medium is always distinguished by a constant pressure at any given level and by a constant temperature. Moreover, because of its vast extent, the medium may receive or give up energy in the form of heat or work without any change in either temperature or pressure.

larly, when  $P_1 < P_0$ , this differential of pressure may be used to do work on a piston as the pressure of the system gradually rises to the dead-state pressure.

We may therefore say that, for any state of the system, the maximum work that can be produced by the system and the medium, as the former changes to its dead state, cannot be less than zero. This maximum work, when obtained without the aid of other than cyclic changes on the part of external systems other than the medium, is called the *availability* which corresponds to that state; the availability which corresponds to the dead state is zero, for all other states must be positive.

It has been shown (Art. 5:3) that maximum work is always associated with the reversible process. During any change in state of the system toward its dead state, the availability will always decrease. If a reversible process that connects the initial and final states is applied, the maximum amount of work which might have been released to external systems other than the medium as the result of interaction between the system and the medium during this change in state may be calculated; that amount of work will represent the decrease in availability of the system (in combination with that medium) as a result of the change in state. Conversely, if the change is away from the dead state and therefore toward greater availability, it is required that energy must have entered the system from external systems other than the medium. If this change in state is reversibly accomplished, the amount of work which the system has *constructively* received in the course of the process from external systems other than the medium will be a minimum (*i.e.*, with respect to the system, a positive-work maximum) and will represent the *increase* of availability that has taken place. The word “constructively,” as used in the foregoing sentence, means that that portion of the heat received by the system during the process which could have been converted into work if supplied to a Carnot engine that has either the system or the medium as its source (depending upon which is at the higher temperature) and the other as its refrigerator must be counted as work. The constructive work of a reversible process that connects states of equal availability is, of course, zero.

In order to calculate the change in availability that accompanies a change in state, it will be necessary to evaluate the maximum amount of work that can be developed by interaction between the system and the medium as the system changes from state 1 at the beginning of a given process to state 2 at the end of that process; this, as stated above, is determined by assuming the change in state to have taken place reversibly. During an infinitesimal section of this assumed reversible process there may be an infinitesimal heat flow  $\partial Q$  and an infinitesimal flow of energy in the form of work,  $\partial W$ . Both  $\partial Q$  and  $\partial W$  are expressed, in sign,



with reference to the system. If, during this infinitesimal step, the temperature of the system is below that of the medium, the sign of  $\partial Q$  is positive;  $\partial Q$  is negative in sign if the temperature of the system exceeds that of the medium. If the pressure of the system is greater than that of the medium,  $\partial W$  is positive, and vice versa.

Let us first consider the work that may be delivered to external systems by reason of a heat flow between system and medium. If the temperature  $T$  of the system is above that of the medium during this infinitesimal part of the entire process and if this heat  $\partial Q$  had been supplied a Carnot engine, the work delivery of that engine would have been  $-\partial Q(T - T_0)/T$ , the minus sign having been given  $\partial Q$  since the direction of heat flow with respect to the engine is opposite to its direction with respect to the system. If, on the other hand,  $T$  is less than  $T_0$ , the heat supplied the Carnot engine will come from the medium and will be equal to  $\partial Q(T_0/T)$ , where  $\partial Q$  is still the heat flow with respect to the system. The work output of the Carnot engine will, in that case, be  $\partial Q \frac{T_0}{T} \frac{T_0 - T}{T_0} = -\partial Q \frac{T - T_0}{T}$ , thus being represented by the same expression that resulted from the opposite assumption. Moreover, this expression must give a positive result, indicating that work was delivered to external systems, whenever  $T$  differs from  $T_0$ ; for if  $T > T_0$ ,  $\partial Q$  is negative, and if  $T < T_0$ ,  $\partial Q$  is positive.

To obtain the total work deliverable to external systems, account must also be taken of  $\partial W$ , the work flow during this infinitesimal part of the reversible process. This  $\partial W$  is, of course, the gross work of the process and not the net work deliverable to external systems other than the medium; it is the net work in which we are interested. If the pressure  $P$  of the system is above  $P_0$ , the system will expand and the work done by the system on the medium as the result of this expansion is  $P_0 dV$ ; if  $P < P_0$ ,  $dV$  is negative, the work done by the system on the medium is negative but, since  $dV$  is negative, still may be expressed as  $P_0 dV$ . We may therefore write for the net work deliverable to external systems,  $\partial W - P_0 dV$ .

Adding the work deliverable by reason of a pressure difference between system and medium to that obtainable because of a temperature difference, we have

$$\begin{aligned} -\partial Q \frac{T - T_0}{T} + \frac{\partial W}{J} - \frac{P_0 dV}{J} &= -\left(1 - \frac{T_0}{T}\right) \partial Q + \frac{\partial W}{J} - \frac{P_0 dV}{J} \\ &= -\partial Q + \frac{\partial W}{J} - \frac{P_0 dV}{J} + T_0 \frac{\partial Q}{T} \end{aligned}$$

But, from Eq. (2:4),  $-\partial Q + \partial W/J = -dE$ ; also, since this is a reversible process, we may substitute  $dS$  for  $\partial Q/T$ . Thus the maximum work

deliverable to external systems during this infinitesimal process is

$$-dE - \frac{P_0 dV}{J} + T_0 dS$$

Since the pressure  $P_0$  and the temperature  $T_0$  of the medium do not change, this may be extended to cover a finite change of state, as follows,

$$-\Delta E - \frac{P_0 \Delta V}{J} + T_0 \Delta S$$

and the maximum possible amount of work that can be delivered to external systems is therefore the decrease in the quantity

$$E + \frac{P_0 V}{J} - T_0 S \quad (16:1)$$

Because this maximum amount of work measures the availability corresponding to a given state of the system, the foregoing expression will be called the *availability function*. It is not a property of the system alone, being expressed in terms of system properties and the temperature and pressure of the medium.

The availability of a system at a given state may be measured as the change in the value of the availability function as the system changes from that state to its dead state. At this dead state, the properties of the system will be designated by the subscript 0, and we may write

$$\text{Availability} = \left( E + \frac{P_0 V}{J} - T_0 S \right) - \left( E_0 + \frac{P_0 V_0}{J} - T_0 S_0 \right) \quad (16:2)$$

This expression cannot, for any state of the system, have a lower value than zero.<sup>1</sup> The *change* of availability as the system changes from state 1 to state 2 is the change in the value of the availability function between the two states, or

$$\Delta(\text{Availability}) = \left( E_2 + \frac{P_0 V_2}{J} - T_0 S_2 \right) - \left( E_1 + \frac{P_0 V_1}{J} - T_0 S_1 \right) \quad (16:3)$$

This change in availability may be either positive, indicating an increase in availability, or negative, if the system, in combination with the medium, is less capable of delivering work to external systems as it changes to the dead state.

When the system is a simple system, energy storage by reason of motion, elevation, magnetism, or electricity being negligible,  $U$  may, of course, replace  $E$  in the foregoing expressions. For the simple system, the sym-

<sup>1</sup> The *availability function* may have a value less than zero, but its value at the dead state is its lowest possible value.



bol  $\beta$  will be used to designate the value of the availability function as it applies to a unit weight, or

$$\beta = u + \frac{P_0 v}{J} - T_0 s \quad (16:4)$$

*Example 16:2.* In combination with an atmosphere at 14 psia, 70°F, calculate the availability of 1 lb of H<sub>2</sub>O at a pressure of 200 psia and in the following states: (a) 500°F; (b) saturated vapor; (c) saturated liquid; (d) 70°F; (e) 32°F.

*Solution.* The  $\beta$  function will represent the availability function for this simple system. In the dead state, the water has a pressure and temperature corresponding to those of the atmosphere. It is thus a compressed liquid but, for simplicity of calculation, will be assumed incompressible. This means that its volume, internal energy, and entropy are the same as those of the saturated liquid at the same temperature. Thus, at  $p = 14.7$  psia,  $t = 70^\circ\text{F}$ ,

$$u_0 = u_f = h_f - \frac{(P - P_{\text{sat}})v_f}{J} = 38.04 - \frac{(144)(14.7 - 0.36)(0.01606)}{778} = 38.00 \text{ Btu}$$

$$v_0 = 0.01606; s_0 = 0.0745$$

$$\beta_0 = u_0 + \frac{P_0 v_0}{J} - T_0 s_0 = 38.00 + \frac{(144)(14.7)(0.01606)}{778} - (530)(0.0745) = 38.00 + 0.04 - 39.49 = -1.45 \text{ Btu}$$

(a) This is a superheated steam condition.

$$u = h - \frac{Pv}{J} = 1268.9 - \frac{(144)(200)(2.726)}{778} = 1168.0 \text{ Btu}$$

$$\beta = 1168.0 + \frac{(144)(14.7)(2.726)}{778} - (530)(1.6240) = 1168.0 + 7.4 - 860.7 = 314.7 \text{ Btu}$$

$$\text{Availability} = \beta - \beta_0 = 314.7 - (-1.45) = 316.1 \text{ Btu}$$

$$(b) \beta = 1113.7 + \frac{(144)(14.7)(2.288)}{778} - (530)(1.5453) = 300.9 \text{ Btu}$$

$$\text{Availability} = 300.9 - (-1.45) = 302.3 \text{ Btu}$$

$$(c) \beta = 354.68 + \frac{(144)(14.7)(0.01839)}{778} - (530)(0.5435) = 66.68 \text{ Btu}$$

$$\text{Availability} = 66.68 - (-1.45) = 68.13 \text{ Btu}$$

$$(d) u = u_0 = 38.00; v = v_0 = 0.01606; s = s_0 = 0.0745$$

$$\beta = \beta_0 = -1.45 \text{ Btu; availability} = 0$$

This result is slightly misleading, though correct as based on the assumption of incompressibility. If compressibility had been taken into account,  $\beta$  would have been very slightly larger (less negative) than  $\beta_0$  and the availability would have been positive. The number of places to which the values of the properties are shown in the steam tables would hardly have been sufficient to show this difference.

$$(e) \beta = 0.00 + \frac{(144)(14.7)(0.01602)}{778} - (530)(0.00) = 0.04 \text{ Btu}$$

$$\text{Availability} = 0.04 - (-1.45) = 1.49 \text{ Btu}$$

Note that positive availability is shown although the temperature of the system is below the temperature of the atmosphere.

**16:3. The Evaluation of Irreversibility.** There have been occasions in earlier chapters when we were concerned with the evaluation of irreversibility. For example, comparisons have been made between the efficiency of a heat engine, or a heat-engine cycle, and the efficiency of its equivalent Carnot cycle; the refrigerating efficiency introduced in Chap. 15 is another example. Both of these developed as the ratio of realized to perfect performance and applied to the *cycle as a whole*. Engine (or turbine) efficiency was, on the other hand, an attempt to express the irreversibility of one of the *processes* of the cycle in the form of a similar ratio.

We shall now introduce a method of evaluating the irreversibility of a process in terms of the difference between the amount of useful work which might have been delivered as the system changed between the end states of the process if that process had been reversibly performed and the work that was actually (though sometimes, at least in part, constructively) delivered during the real process. The maximum work that is associated with the reversible process has been shown to be equal to the decrease of availability; for an infinitesimal segment of the entire process, it is  $-dE - P_0 dV/J + T_0 dS$ . In calculating the constructive work of the real process, we may first set down the work actually delivered as useful work performed on external systems other than the medium. This is  $\partial W - P_0 dV$  and will be designated as  $\partial W_u$ . To this useful work must be added the work constructively received by these external systems due to the amount of heat they have received; if this heat  $\partial Q$  had been supplied a Carnot engine having the medium as its sink, the work realized would have been  $-\partial Q(T - T_0)/T$ , where  $T$  is the temperature of the system as this minute step is taken. Note that it has been shown in Art. 16:2 that, if the temperature  $T$  is below  $T_0$ , this expression will still be valid. The total constructive work of the real, though infinitesimal, process is therefore  $\partial W_u/J - \partial Q(T - T_0)/T$ , and we may write

$d(\text{Irreversibility})$

$$\begin{aligned} &= \left( -dE - \frac{P_0 dV}{J} + T_0 dS \right) - \left( \frac{\partial W_u}{J} - \partial Q \frac{T - T_0}{T} \right) \\ &= \left( \partial Q \frac{T - T_0}{T} - \frac{\partial W_u}{J} \right) - d \left( E + \frac{P_0 V}{J} - T_0 S \right) \quad (16:5) \end{aligned}$$

The irreversibility encountered in the course of the entire process may be evaluated by integrating this expression, or

$$\text{Irreversibility} = \left( \int_1^2 \frac{T - T_0}{T} \partial Q - \frac{{}_1W_{u2}}{J} \right) - \Delta(\text{availability}) \quad (16:6)$$



An expression for irreversibility that is sometimes easier to use than Eq. (16:6) may be obtained from that equation by writing it in the form

$$\begin{aligned}\text{Irreversibility} &= \int_1^2 \partial Q - T_0 \int_1^2 \frac{\partial Q}{T} - \frac{{}_1W_{u2}}{J} \\ &\quad - \left[ E_2 - E_1 + \frac{P_0(V_2 - V_1)}{J} - T_0(S_2 - S_1) \right] \\ &= {}_1Q_2 - T_0 \int_1^2 \frac{\partial Q}{T} - (E_2 - E_1) - \frac{{}_1W_{u2} + P_0(V_2 - V_1)}{J} \\ &\quad + T_0(S_2 - S_1)\end{aligned}$$

Or, since  ${}_1W_{u2} + P_0(V_2 - V_1) = {}_1W_2$  and  ${}_1Q_2 = E_2 - E_1 + {}_1W_2/J$ ,

$$\text{Irreversibility} = T_0(S_2 - S_1) - T_0 \int_1^2 \frac{\partial Q}{T} \quad (16:7)$$

Equations (16:6) and (16:7) will both find use in measuring the irreversibility of the closed system during a nonflow process. The irreversibility can never be negative as that would imply that the process had been more perfectly performed than a reversible process which connects the same end states.

*Example 16:3.* The temperature and pressure of the atmosphere are 70°F and 14.7 psia, respectively. The system consists of 1 lb of steam, originally at 200 psia, 500°F. Calculate the change of availability and the irreversibility which accompany the following processes: (a) The system, while confined behind a piston at constant pressure, expands slowly as its temperature is increased to 600°F by the addition of heat. (b) The same change of state as in part *a* is effected without heat flow, as the result of a paddle-wheel process. (c) The system expands adiabatically and reversibly to a pressure of 14.7 psia. (d) It expands adiabatically into an adjoining space which is initially empty. The final pressure is 14.7 psia. (e) It expands adiabatically to become a saturated vapor at 14.7 psia.

*Solution.* The  $\beta$  function becomes the availability function for this simple system.  $\beta_1$  has been calculated as 314.7 Btu in Example 16:2, part *a*.

$$(a) \ u_2 = 1322.1 - \frac{(144)(200)(3.060)}{778} = 1208.8 \text{ Btu}$$

$$\beta_2 = 1208.8 + \frac{(144)(14.7)(3.060)}{778} - (530)(1.6767) = 328.4 \text{ Btu}$$

$$\Delta(\text{Availability}) = \beta_2 - \beta_1 = 328.4 - 314.7 = 13.7 \text{ Btu}$$

In Eq. (16:7),

$$\int_1^2 \frac{\partial Q}{T} = \int_1^2 \frac{dh}{T} = \int_1^2 c_p \frac{dT}{T} = s_2 - s_1$$

$$\text{Irreversibility} = T_0(s_2 - s_1) - T_0(s_2 - s_1) = 0$$

(b)  $\Delta(\text{Availability}) = 13.7 \text{ Btu}$  from part *a*

In Eq. (16:7),

$$\partial Q = 0$$

$$\text{Irreversibility} = T_0(s_2 - s_1) - 0 = 530(1.6767 - 1.6240) = 28.0 \text{ Btu}$$

This means that the net work of stirring was  $28.0 + 13.7 = 41.7 \text{ Btu}$ .

Checking,

$$\begin{aligned} \text{Net work} &= h_2 - h_1 - \frac{(P - P_0)(v_2 - v_1)}{J} \\ &= 1322.1 - 1268.9 - \frac{144(200 - 14.7)(3.060 - 2.726)}{778} = 41.7 \text{ Btu} \end{aligned}$$

(c) Using the Mollier diagram, the final condition is located at  $x_2 = 0.908$ ;  $u_2 = 180.0 + (0.908)(897.5) = 995.0 \text{ Btu}$ ;  $v_2 = (0.908)(26.80) = 24.34$ ;  $s_2 = s_1 = 1.6240$ .

$$\beta_2 = 995.0 + \frac{(144)(14.7)(24.34)}{778} - (530)(1.6240) = 200.5 \text{ Btu}$$

$$\Delta(\text{Availability}) = \beta_2 - \beta_1 = 200.5 - 314.7 = -114.2 \text{ Btu}$$

In Eq. (16:7),

$$\partial Q = 0 \text{ and } s_2 - s_1 = 0$$

$$\text{Irreversibility} = 0$$

This means that 114.2 Btu of useful work resulted from the expansion.

Checking,

$$\frac{{}_1W_2}{J} = u_1 - u_2 = 1168.0 - 995.0 = 173 \text{ Btu}$$

$$\frac{{}_1W_{u2}}{J} = \frac{{}_1W_2}{J} - \frac{P_0(v_2 - v_1)}{J} = 173.0 - \frac{(144)(14.7)(24.34 - 2.726)}{778} = 114.2 \text{ Btu}$$

(d) There is no work and no heat flow. Therefore, for this nonflow expansion,  $u_2 = u_1 = 1168 \text{ Btu}$ . Using information from Table 3 of the steam tables, the final state is located as corresponding to a temperature  $t_2$  of approximately  $463^\circ\text{F}$ . Also,  $v_2 = 37.27$ , and  $s_2 = 1.9075$ . Then

$$\beta_2 = 1168.0 + \frac{(144)(14.7)(37.27)}{778} - (530)(1.9075) = 258.3 \text{ Btu}$$

$$\Delta(\text{Availability}) = \beta_2 - \beta_1 = 258.3 - 314.7 = -56.4 \text{ Btu}$$

Using Eq. (16:7),

$$\text{Irreversibility} = T_0(s_2 - s_1) - 0 = 530(1.9075 - 1.6240) = 150.1 \text{ Btu}$$

The difference between the irreversibility and the decrease of availability is  $150.1 - 56.4 = 93.7 \text{ Btu}$ . Checking, it will be found that this was the amount of work required to evacuate the atmosphere from the space into which the expansion took place and thus was required from external systems preparatory to the execution of the designated process.

$$(e) \beta_2 = 1077.5 + \frac{(144)(14.7)(26.80)}{778} - (530)(1.7566) = 219.4 \text{ Btu}$$

$$\Delta(\text{Availability}) = \beta_2 - \beta_1 = 219.4 - 314.7 = -95.3 \text{ Btu}$$

From Eq. (16:7),

$$\text{Irreversibility} = T_0(s_2 - s_1) - 0 = 530(1.7566 - 1.6240) = 70.3 \text{ Btu}$$

For this adiabatic process, the difference between the decrease of availability and the irreversibility should equal the useful work.



Checking,

$$\frac{{}_1W_2}{J} = u_1 - u_2 = 1168.0 - 1077.5 = 90.5$$

$$\frac{{}_1W_{u_2}}{J} = {}_1W_2 - \frac{P_0(v_2 - v_1)}{J} = 90.5 - \frac{(144)(14.7)(26.80 - 2.726)}{778} = 25.0$$

$$= 95.3 - 70.3$$

**16:4. Availability in Steady Flow.** Most real engineering processes are essentially steady-flow processes. The availability in steady flow includes the work which can be delivered to external systems other than the medium by reason of that flow. This increment of useful work is the difference between the work required to displace the fluid across the section at which the availability is to be measured (the flow work of Chap. 3) and the amount of that work if the volume displaced had been the same but the pressure had been that of the medium; it is thus equal, per pound of fluid flowing, to  $Pv - P_0v$ . Returning to Eq. (16:2) and making this addition to the availability of a unit weight, we have

$$\begin{aligned} \text{Availability per lb} &= \left( e + \frac{P_0v}{J} - T_0s \right) - \left( e_0 + \frac{P_0v_0}{J} - T_0s_0 \right) \\ &\quad + \frac{Pv - P_0v}{J} \\ &= \left( e + \frac{Pv}{J} - T_0s \right) - \left( e_0 + \frac{P_0v_0}{J} - T_0s_0 \right)^* \end{aligned} \quad (16:8)$$

If energy storage due to capillarity, magnetism, or electricity is negligible,  $e = u + \bar{V}^2/2Jg + z/J$  and

$$\begin{aligned} \text{Availability per lb} &= \left( u + \frac{Pv}{J} - T_0s + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) \\ &\quad - \left( u_0 + \frac{P_0v_0}{J} - T_0s_0 + \frac{\bar{V}_0^2}{2Jg} + \frac{z_0}{J} \right) \end{aligned}$$

But  $u + Pv/J = h$  and  $\bar{V}_0$  is zero (see footnote, page 387). Therefore

$$\begin{aligned} \text{Availability per lb} &= \left( h - T_0s + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) - \left( h_0 - T_0s_0 + \frac{z_0}{J} \right) \\ &= \left( b + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) - \left( b_0 + \frac{z_0}{J} \right) \end{aligned} \quad (16:9)$$

where

$$b = h - T_0s \quad (16:10)$$

Like the availability function developed in Art. 16:2,  $b$  is a combination function of the properties of the system and the medium. It cannot,

\* Note that the availability in steady flow may be negative if the pressure of the substance is less than that of the medium.

however, be called a steady-flow availability function, since the latter must include the energy quantities that are expressed in terms of the velocity and the elevation, or

$$\text{Availability function, steady flow} = b + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \quad (16:11)$$

Thus the change in availability in steady flow, as the flow progresses from section 1 to section 2, is

$$\begin{aligned} \Delta(\text{Availability, steady flow}) = & \left( b_2 + \frac{\bar{V}_2^2}{2Jg} + \frac{z_2}{J} \right) \\ & - \left( b_1 + \frac{\bar{V}_1^2}{2Jg} + \frac{z_1}{J} \right) \end{aligned} \quad (16:12)$$

**16:5. Irreversibility in Steady Flow.** In evaluating the irreversibility of a steady-flow process, the basis of evaluation is the same as for the closed-system process, the work constructively delivered to external systems in the course of the process being deducted from the decrease of availability that has resulted. Thus

$$\begin{aligned} \text{Irreversibility, steady flow} = & \int_1^2 \left( \frac{T - T_0}{T} \right) \partial Q - \frac{{}_1W_2}{J} \\ & - \Delta(\text{availability, steady flow}) \end{aligned} \quad (16:13)$$

where  ${}_1W_2$  has the same meaning as in the steady-flow *energy equation* [Eq. (3:5)] and is the work delivered to external systems other than the medium as the result of the real steady-flow process. Both  ${}_1W_2$  and  $\partial Q$  in this equation are expressed in sign with respect to the system, so that a flow of work from the system is positive, a flow of heat negative. Although the steady-flow availability may conceivably be negative, irreversibility in steady flow can never be less than zero.

*Example 16:5A.* A steady stream of  $\text{H}_2\text{O}$  at 200 psia,  $500^\circ\text{F}$ , enters the following steady-flow processes at negligible velocity. The pressure and temperature of the atmosphere are 14.7 psia and  $70^\circ\text{F}$ . Calculate, for each process, the change of availability and the irreversibility, per pound of  $\text{H}_2\text{O}$ . (a) The stream is heated slowly at constant pressure until its temperature is  $600^\circ\text{F}$ . (b) It expands adiabatically and reversibly through a nozzle to 14.7 psia. (c) It is throttled to 14.7 psia, the final velocity being negligible.

*Solution:*

$$h_1 = 1268.9; s_1 = 1.6240; b_1 = 1268.9 - (530)(1.6240) = 408.2 \text{ Btu}$$

$$(a) h_2 = 1322.1; s_2 = 1.6767; b_2 = 1322.1 - (530)(1.6767) = 433.4 \text{ Btu.}$$

$$\Delta(\text{Availability}) = b_2 - b_1 = 433.4 - 408.2 = 25.2 \text{ Btu}$$

There is no irreversibility. In Eq. (16:13),  ${}_1W_2$  is zero, but  $\int_1^2 \frac{T - T_0}{T} \partial Q$ , when evaluated, will equal 25.2 Btu. This may be checked, approximately, as follows:



The system receives  $1322.1 - 1268.9$  Btu of heat at an average temperature of  $550^\circ\text{F}$ . If this amount of heat were supplied at that temperature to a Carnot engine with a  $70^\circ\text{F}$  sink, the work output of that engine would be  $53.2(550 - 70)/(550 + 460) = 25.3$  Btu. Thus the work *constructively* furnished by external systems accounts for the increase in availability, confirming the reversibility of the process.

(b) From Example 16:3,  $x_2 = 0.908$ .  $h_2 = 180.07 + (0.908)(970.3) = 1061.1$  Btu;  $s_2 = s_1 = 1.6240$ ;  $b_2 = 1061.1 - (530)(1.6240) = 200.4$  Btu. The availability function as expressed for the nozzle exit must also include the kinetic energy term  $\bar{V}_2^2/2Jg = h_1 - h_2 = 1268.9 - 1061.1 = 207.8$  Btu. Then

$$\Delta(\text{Availability}) = b_2 + \frac{\bar{V}_2^2}{2Jg} - b_1 = 200.4 + 207.8 - 408.2 = 0$$

This value is in accordance with the fact that there has been no exchange of energy with external systems either as heat or as work and with the description of the process as reversible.

(c)  $h_1 = 1268.9 = h_2$ . At 14.7 psia, this enthalpy corresponds to a temperature of approximately  $462^\circ\text{F}$  and  $s_2 = 1.9070$ ;  $b_2 = 1268.9 - (530)(1.9070) = 258.2$  Btu.

$$\Delta(\text{Availability}) = b_2 - b_1 = 258.2 - 408.2 = -150.0 \text{ Btu}$$

There has been no heat flow or useful work. Applying Eq. (16:13), the irreversibility is therefore the decrease of availability, or  $+150.0$  Btu.

It is remembered that the various items of equipment in an engineering plant usually operate to accomplish certain changes in the condition of the fluid while the latter is in essentially steady flow. Equation (16:13) may then be applied to each unit in turn, and each unit may thereby be charged with its proper portion of the blame for any failure of the entire plant to show a perfect performance of its function. In large proportion, the various pieces of apparatus that operate on the fluid in the engineering plant may be grouped as belonging either to the engine classification or in the category of heat exchangers.

The class of apparatus to which the engine belongs (and this includes turbines and compressors) carries out a process which is essentially adiabatic, even though not reversible, in character, and  $\partial Q$  in Eq. (16:13) is therefore zero. This simplifies the calculation of the irreversibility encountered in the type of process carried out by this group to a simple subtraction of the useful work delivered from the decrease of availability. When the unit is a compressor, an increase of availability is usually detected but in this case the work is negative, so that the irreversibility will be characteristically positive as for the engine.

*Example 16:5B.* The temperature and pressure of the atmosphere are  $70^\circ\text{F}$  and 14.7 psia. Steam at 200 psia,  $500^\circ\text{F}$ , enters a turbine at low velocity and is expanded to 14.7 psia. The turbine has an efficiency of 70 per cent, and the exit velocity is negligible. Calculate the change of availability per pound of steam and the irreversibility of the turbine process.

*Solution:*

$$h_1 = 1268.9; s_1 = 1.6240; b_1 = 408.2 \text{ Btu}$$

[Ex. 16:5A]

At the end of an isentropic expansion to 14.7 psia, the enthalpy is 1061.1 Btu. Then

$$h_2 = 1268.9 - 0.70(1268.9 - 1061.1) = 1123.4 \text{ Btu}$$

$$x_2 = \frac{1123.4 - 180.07}{970.3} = 0.972; s_2 = 0.3120 + (0.972)(1.4446) = 1.716$$

$$b_2 = 1123.4 - (530)(1.716) = 213.9 \text{ Btu}$$

$$\Delta(\text{Availability}) = b_2 - b_1 = 213.9 - 408.2 = -194.3 \text{ Btu}$$

There has been no heat flow. The useful work equals the decrease of enthalpy, or  $1268.9 - 1123.4 = 145.5$  Btu. Substituting in Eq. (16:13),

$$\text{Irreversibility} = -145.5 - (-194.3) = 48.8 \text{ Btu}$$

Heat exchangers may, for our purpose, be divided into two subclasses, but for neither of these subclassifications is any significant amount of useful work performed; the main objective is the transfer of heat. Thus, in Eq. (16:13),  ${}_1W_2$  is zero, and we may ignore it in the calculation of irreversibility. The first kind of heat exchanger accomplishes its purpose by mixing two or more streams of fluid; ultimately, this flowing mixture may again divide into separate streams. If it is assumed that the only exchange of heat has been between the fluids of these streams, this can also be made an adiabatic process when we include in the system all of the streams. Thus  $\partial Q$ , as well as  ${}_1W_2$ , has a zero value in Eq. (16:13), and the calculation of the irreversibility of the process becomes a summing of the availabilities of all of the entering streams and of all the outgoing streams and a subtraction of the second total from the first. The relative mass rates of flow in the various streams must, of course, be taken into account in applying Eq. (16:13) and, for the heat exchanger,

$$\text{Irreversibility} = \sum_i M \left( b + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) - \sum_o M \left( b + \frac{\bar{V}^2}{2Jg} + \frac{z}{J} \right) \quad (16:14)$$

in which  $\sum_i$  represents the summation of all incoming streams and  $\sum_o$  the corresponding summation for those outgoing.

The second class of heat exchangers keeps the streams of fluid separate as heat is passed between them through surfaces such as the walls of tubes. When Eq. (16:13) is applied to each stream separately, there will be a flow of heat, although no useful work is involved; the irreversibility, as calculated by Eq. (16:13), will be zero. However, the total increase of availability for those streams which are receiving heat will be less than the decrease of availability for the streams which are supplying this heat. Considering all streams to constitute a single system, the process is again an adiabatic as well as a no-work process, and Eq. (16:14) may be used to evaluate the irreversibility of the heat-exchange process:



*Example 16:5C.* The steam exhausted from the turbine of Example 16:5B is condensed at constant pressure to a saturated liquid in a surface condenser. Cooling water enters this condenser at 70°F and leaves at 130°F. Its velocity may be assumed negligible. Per pound of wet steam entering the condenser, calculate (a) the change of availability and the irreversibility that accompanies the condensation of the steam, (b) the change of availability and the irreversibility that accompanies the heating of the cooling water, and (c) the irreversibility of the process as a whole.

*Solution:*

(a) From Example 16:5B, the enthalpy  $h_1$  of the steam as it enters the condenser is 1123.4 Btu, and  $b_1 = 213.9$  Btu. As a saturated liquid at the same pressure,  $h_2 = 180.07$  Btu and  $b_2 = 180.07 - (530)(0.3120) = 14.7$  Btu.

$$\Delta(\text{Availability}) = b_2 - b_1 = 14.7 - 213.9 = -199.2 \text{ Btu}$$

In Eq. (16:13),  ${}_1W_2 = 0$  and  $\int_1^2 \frac{T - T_0}{T} \partial Q$  may be evaluated on the basis of the constant temperature at which condensation took place, or  $212 + 460 = 672^\circ\text{R}$ . The total heat flow from the steam as it condensed was  $h_2 - h_1 = 180.07 - 1123.4 = -943.3$  Btu. Thus

$$\int_1^2 \frac{T - T_0}{T} \partial Q = -943.3 \left( \frac{672 - 530}{672} \right) = -199.2 \text{ Btu}$$

and, from Eq. (16:13),

$$\text{Irreversibility} = -199.2 - (-199.2) = 0$$

(b) The heat absorbed by 1 lb of cooling water is equal to its change of enthalpy. Although this water actually carries an overpressure, the effect on its enthalpy is negligible and the values for saturated water will be used. Thus

$${}_1Q_2 = h_{f_2} - h_{f_1} = 97.90 - 38.04 = 59.86 \text{ Btu per pound cooling water}$$

$$\text{Weight of cooling water per pound of steam condensed} = M = \frac{943.3}{59.86} = 15.75 \text{ lb}$$

$$b_1 = 38.04 - (530)(0.0745) = -0.45 \text{ Btu}; b_2 = 97.90 - (530)(0.1816) = 1.65 \text{ Btu}$$

$$\Delta(\text{Availability}) = M(b_2 - b_1) = 15.75[1.65 - (-0.45)] = 33.1 \text{ Btu}$$

This process, considered alone, also shows no irreversibility, for if  $\int_1^2 \frac{T - T_0}{T} \partial Q$  is evaluated, it may be shown to have a value of 33.1 Btu and since  ${}_1W_2 = 0$ , Eq. (16:13) gives

$$\text{Irreversibility} = 33.1 - 33.1 = 0$$

(c) For the process as a whole, there has been no transfer of energy to or from external systems either as heat or as work. The transfer of energy in this case is between parts of what is now the same system. The irreversibility of the process as a whole is equal to the decrease of availability of that system, or

$$\text{Irreversibility} = -\Delta(\text{availability}) = -(-199.2 + 33.1) = 166.1 \text{ Btu}$$

As an alternate method, Eq. (16:14) may be used.

$$\begin{aligned} \text{Irreversibility} &= [(1)(213.9) + (15.75)(-0.45)] - [(1)(14.7) + (15.75)(1.65)] \\ &= 166.1 \text{ Btu} \end{aligned}$$

This irreversibility of the process as a whole reflects the effect of the finite difference in temperature between the steam and the cooling water. This temperature interval did not enter into the calculation when the two streams were considered individually.

Apparatus which carries out a throttling process, as in the throttle-governing of engines or turbines or the expansion valve of the vapor-compression refrigerating plant, is sometimes used in engineering plants. These are no-heat no-work processes, and the irreversibility is equal to the decrease of availability. An illustration will be found in Example 16:5A, part *c*.

**16:6. Efficiency versus Effectiveness of the Turbine Stage.** The efficiency of a turbine stage has been defined in Art. 11:13 as the ratio of the actual enthalpy drop across the stage to the isentropic drop that would have been obtained if the expansion had been reversibly, as well as adiabatically, performed. In Fig. 16:1, a Mollier diagram, the expan-

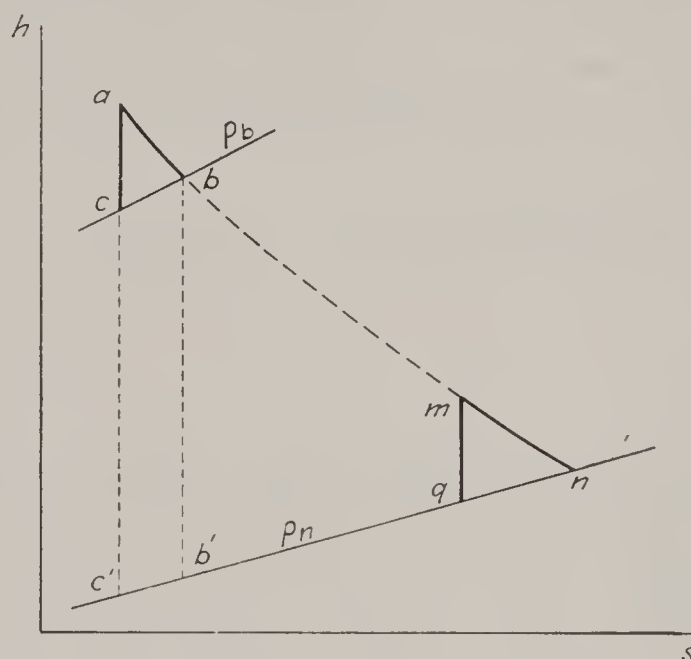


FIG. 16:1. Stage efficiency vs. stage effectiveness.

sion in a high- and a low-pressure stage of the same real turbine has been represented by the lines  $ab$  and  $mn$ , respectively. The expansions in reversible stages from the same initial states  $a$  and  $m$  to the same final stage pressures  $p_b$  and  $p_n$  are shown as  $ac$  and  $mq$ . These have, for the purpose of convenient comparison in the analysis to follow, been made equal in length. Also, for the same reason the efficiencies of these two stages have been assumed to be the same.

The efficiency of the high-pressure stage is  $(h_a - h_b)/(h_a - h_c)$ , and the work performed in that stage is  $h_a - h_b$ , per pound of fluid flow; this assumes that there is no significant difference in velocity or elevation of the fluid between stage entrance and exit. At first thought, the irreversibility of this stage would seem to be equal to the unrealized drop of enthalpy,  $h_b - h_c$ . But the fluid leaves the real stage at state  $b$ , the isentropic stage at state  $c$ . The isentropic, or ideal, expansion to condenser pressure  $p_n$  from state  $b$  will produce work in the amount  $h_b - h_{b'}$ , while an expansion from state  $c$  to the same pressure will develop  $h_c - h_{c'}$ , a smaller amount of work because of the divergence of constant-pressure



lines  $p_b$  and  $p_n$ . In other words, the decrease of availability has not been as large for the real stage as for the isentropic stage, and although the work in the real stage is less than the decrease of availability in that stage while, in the isentropic stage, these two quantities are equal, the picture is not quite as dark as it is painted by the value which we call the stage efficiency; some of the apparently lost work  $h_b - h_c$  is recoverable in later expansion.

The *effectiveness* of a turbine stage gives a more accurate picture of the effect of the irreversibilities encountered in a single turbine stage on the performance of the turbine as a whole. Effectiveness is expressed as the ratio the work performed in the real stage bears to the decrease of availability that has taken place in that stage. The work of the high-pressure stage of Fig. 16:1 is  $h_a - h_b$ ; making the same assumption with regard to equality of fluid velocity and elevation at entrance to and exit from the stage that has been the basis of the accepted expression for stage efficiency, the decrease of availability in this stage is  $b_a - b_b$ , and the effectiveness of the stage is  $(h_a - h_b)/(b_a - b_b)$ . This may be compared with  $(h_a - h_b)/(h_a - h_c)$ , the stage efficiency, as follows:

$$b_a - b_b = (h_a - T_0 s_a) - (h_b - T_0 s_b) = h_a - h_b + T_0(s_b - s_a)$$

In the real stage,  $s_b$  is always greater than  $s_a$ , and  $T_0$  cannot be negative; thus  $T_0(s_b - s_a)$  is always a positive quantity. If this quantity is smaller than the positive difference of enthalpy,  $h_b - h_c$ , then  $(b_a - b_b) < (h_a - h_c)$  and the stage effectiveness will exceed the stage efficiency. The difference of enthalpy  $h_b - h_c$  is equal to the heat flow required to change the state of unit weight of the fluid from  $c$  to  $b$  at constant pressure  $p_b$  and therefore to  $\int_c^b T ds$ , where  $T$  is the (possibly variable) temperature along the constant-pressure path  $cb$ . If the temperature between the points  $c$  and  $b$  is everywhere above  $T_0$ , as it always is in any stage of a real turbine, then  $\int_c^b T ds > T_0(s_b - s_c)$ . But  $s_c = s_a$  and  $T_0(s_b - s_a)$  may be substituted for  $T_0(s_b - s_c)$  in this inequality; also,  $h_b - h_c$  may substitute for  $\int_c^b T ds$ , and the inequality becomes  $(h_b - h_c) > T_0(s_b - s_a)$ . The effectiveness of any real stage will therefore exceed its efficiency. The conventional expressions for stage efficiency and stage effectiveness are

$$\eta_s = \frac{-\Delta h}{-\Delta h_s} \quad (16:15)$$

$$\epsilon_s = \frac{-\Delta h}{-\Delta b} \quad (16:16)$$

where  $\eta_s$  and  $\epsilon_s$  are, respectively, the stage efficiency and effectiveness,  $-\Delta h$  is the drop of enthalpy that takes place in the real stage,  $-\Delta h_s$  is the

isentropic drop of enthalpy between the entrance state and the exit pressure, and  $-\Delta b$  is the decrease of availability between states at entrance to and at exit from the real stage. It is also possible to state that, for any real stage,  $\epsilon_s > \eta_s$ .

Having developed the concept of stage effectiveness from a study of the high-pressure stage of Fig. 16:1, let us apply it to the low-pressure stage of that figure. It will be assumed that this stage exhausts to the condenser, and the initial assumption will also be that the temperature maintained in constant-pressure condensation in the condenser is the temperature  $T_0$  of the atmosphere. In that case it will be noted that  $\int_q^n T ds = T_0(s_n - s_m)$ , that  $b_m - b_n = h_m - h_q$ , and that the efficiency and the effectiveness of the stage are therefore equal. Since the efficiencies of the high- and low-pressure stages are the same by assumption and the effectiveness exceeded the efficiency in the high-pressure stage, this means that the effectiveness of the low-pressure stage is less than that of the high-pressure stage. Although the condenser temperature can never be as low as  $T_0$  in practice and thus the effectiveness will always be greater than the efficiency, it is evident that as the temperature at exit from a stage declines toward the temperature of the atmosphere the difference between the efficiency and the effectiveness will decrease; this decrease will result from an approach of  $-\Delta b$  of Eq. (16:16) toward the  $-\Delta h_s$  of Eq. (16:15).

The irreversibility of a turbine stage is the difference between the drop of availability in the stage and the work of the stage, or  $-\Delta b - (-\Delta h) = \Delta h - \Delta b$ . It has been shown that  $-\Delta b$  becomes a larger fraction of  $-\Delta h_s$  for a stage of given efficiency when the exhaust temperature from the stage is low. Therefore the irreversibility of a low-pressure stage will be greater than that of a high-pressure stage of equal efficiency and having the same isentropic enthalpy drop. We may therefore draw the important conclusion that low efficiency in the high-pressure stages of a turbine has a less serious effect on the efficiency of the turbine as a whole than if the low-pressure stages operate at low efficiency. This conclusion is reflected in the design of real turbines, in which more attention is usually directed toward the reduction of losses in the final stages of expansion than in the early stages.

When the condition line (see Art. 11:14 and Figs. 11:17 and 16:1) is plotted for a turbine that has stages of equal efficiency, a curve will result on the Mollier diagram as shown in Fig. 16:1; if the effectiveness of each stage is the same, the condition line will be straight. In Art. 11:14 it was shown that the efficiency of a multistaged turbine which has equal stage efficiencies will differ from the efficiency of its stages; on the other hand, if the effectiveness of all stages is the same, the over-all effectiveness of the turbine will be identical with that of each of its stages.



*Example 16:6.* Steam enters the first stage of a turbine at 600 psia, 700°F, and leaves the stage at a pressure of 240 psia. The stage efficiency is 70 per cent. The last stage of this turbine receives steam at 5.5 psia,  $x = 0.944$ , and exhausts to the condenser pressure of 1 psia. The efficiency of this stage is also 70 per cent. Atmospheric pressure and temperature are 14.7 psia and 70°F. Velocities at entrance to and exit from each stage will be neglected. Calculate the enthalpy drop, the decrease of availability, the effectiveness, and the irreversibility for (a) the high-pressure stage and (b) the low-pressure stage.

*Solution.* For convenience, the notation of Fig. 16:1 will be used. From the Mollier diagram the following information may be obtained:

$$h_a = 1351; s_a = 1.587 = s_c; h_c = 1251$$

$$h_m = 1077; s_m = 1.749 = s_q; h_q = 977$$

$$(a) -\Delta h = 0.70(h_a - h_c) = 0.70(1351 - 1251) = 70 \text{ Btu/lb}$$

$$h_b = 1351 - 70 = 1281$$

From the Mollier chart, at 240 psia this corresponds to  $s_b = 1.617$ .

$$b_a = 1351 - (530)(1.587) = 510; b_b = 1281 - (530)(1.617) = 424$$

$$\text{Decrease of availability} = -\Delta(\text{availability}) = -\Delta b = 510 - 424 = 86 \text{ Btu/lb}$$

$$\epsilon_s = \frac{-\Delta h}{-\Delta b} = \frac{70}{86} = 0.815$$

$$\text{Irreversibility} = \Delta h - \Delta b = -70 + 86 = 16 \text{ Btu per lb}$$

$$(b) -\Delta h = 0.70(h_m - h_q) = 0.70(1077 - 977) = 70 \text{ Btu}$$

$$h_n = 1077 - 70 = 1007 \text{ Btu}$$

corresponding, at 1 psia, to  $s_n = 1.802$

$$b_m = 1077 - (530)(1.749) = 150; b_n = 1007 - (530)(1.802) = 52$$

$$-\Delta b = 150 - 52 = 98 \text{ Btu/lb}$$

$$\epsilon_s = \frac{70}{98} = 0.715$$

$$\text{Irreversibility} = -70 + 98 = 28 \text{ Btu/lb}$$

It will be observed that the data for the two stages have been so selected that they have equal enthalpy drops as well as equal efficiencies; this permits a direct comparison of their irreversibilities.

### Problems

In the problems to follow, the temperature of the atmosphere will be assumed to be 60°F, its pressure 14.7 psia, except when specifically stated otherwise.

1. Find the availability of 1 lb of H<sub>2</sub>O at a pressure of 100 psia in the following conditions: (a)  $t = 600^\circ\text{F}$ ; (b) saturated vapor; (c) saturated liquid; (d)  $t = 60^\circ\text{F}$ ; (e)  $t = 32^\circ\text{F}$ .

2. Find the availability of 1 lb of H<sub>2</sub>O at a temperature of 500°F in the following states: (a)  $p = 50$  psia; (b)  $p = 14.7$  psia; (c) saturated vapor; (d) saturated liquid; (e)  $p = 500$  psia.

3. Find the availability of 1 lb of air at the following states. Assume the internal energy and the entropy of the air to be referred to (to be zero at) a state in which it is in temperature and pressure equilibrium with the atmosphere. (a)  $p = 100$  psia,  $t = 60^\circ\text{F}$ ; (b)  $p = 100$  psia,  $t = 0^\circ\text{F}$ ; (c)  $p = 100$  psia,  $t = 200^\circ\text{F}$ ; (d)  $p = 100$  psia,  $v = 2 \text{ ft}^3/\text{lb}$ ; (e)  $p = 14.7$  psia,  $t = 60^\circ\text{F}$ ; (f)  $p = 14.7$  psia,  $t = 0^\circ\text{F}$ ; (g)  $p = 14.7$  psia,  $t = 200^\circ\text{F}$ ; (h)  $p = 2$  psia,  $t = 60^\circ\text{F}$ ; (i)  $p = 2$  psia,  $t = 0^\circ\text{F}$ ; (j)  $p = 2$  psia,

$t = 200^\circ\text{F}$ . Would your answers have differed if the internal energy and the entropy had been referred to a different state?

4. Plot a  $\beta s$  chart for steam. Show (a) the saturated-liquid and saturated-vapor lines and the critical point; (b) lines of constant pressure of 4000 psia, 2000 psia, 14.7 psia, and 0.25 in. Hg; (c) lines of constant temperature of 800, 600, 60, and  $32^\circ\text{F}$ ; (d) the triple-point region.

5. Show the appearance of a closed-system (nonflow) Rankine cycle on the chart of Prob. 4. Assume that  $p_u = 200$  psia,  $p_l = 14.7$  psia and (a) that the steam is saturated at the end of the constant-pressure expansion and (b) that its temperature is  $500^\circ\text{F}$  at this point in the cycle.

6. Work Example 16:3 as based on an atmospheric temperature of  $60^\circ\text{F}$ . Comparing with the results of the example, do you find any difference in the changes of availability that take place during the listed processes? Any changes in the calculated irreversibilities? Explain.

7. Work Example 16:3, changing the original state to a saturated vapor at 100 psia and the temperature of the atmosphere to  $60^\circ\text{F}$ .

8. The system consists of 1 lb of saturated steam at 100 psia. Calculate the change of availability and the irreversibility that accompany each of the following processes: (a) While confined in a rigid-walled container, the temperature of the system is raised to  $500^\circ\text{F}$  by the slow addition of heat. (b) The same change of state as in (a) is effected adiabatically, as the result of a paddle-wheel process. (c) The system expands adiabatically into an adjoining space which is initially empty. The final volume is twice the initial volume. (d) The system is originally in turbulent motion, storing kinetic mechanical energy in the amount of 2 Btu. As the result of friction, it comes to rest while still confined within the same rigid-walled container.

9. The system consists of 1 lb of air at 100 psia and  $300^\circ\text{F}$ . Calculate the change of availability and the irreversibility that accompany each of the following processes. Assume the internal energy and the entropy of the air to be zero at a state in which it is in temperature and pressure equilibrium with the atmosphere. (a) The system expands slowly and at constant pressure behind a piston as heat is supplied to it. The final temperature is  $400^\circ\text{F}$ . (b) The same state path as in (a) is followed but as the result of an adiabatic process. (c) The system expands adiabatically and reversibly to a final pressure of 14.7 psia. (d) The system expands adiabatically to a final pressure of 14.7 psia and final temperature of  $60^\circ\text{F}$ . (e) The system expands slowly and reversibly behind a piston at constant temperature to a pressure of 14.7 psia.

10. The system consists of one pound of air at 70 psia and  $200^\circ\text{F}$  and a second pound of air at 15 psia and  $60^\circ\text{F}$ . They are contained in separate compartments of a tank having rigid nonconducting walls. The partition that separates them is punctured, allowing the two bodies of air to mix and reach a common pressure and temperature. Calculate the change of availability of the system and the irreversibility of the process.

11. A pound of nitrogen and a pound of oxygen, both at 14.7 psia and  $60^\circ\text{F}$ , are confined in separate compartments of a container with rigid nonconducting walls. The partition between the two is punctured, allowing the two gases to mix. Calculate the irreversibility of the process.

12. In Prob. 10, assume the partition that separates the two bodies of air to be rigid but to allow the passage of heat. The partition is not punctured, but the two bodies of air reach a common temperature. (a) For the system as described in Prob. 10, calculate the change of availability and the irreversibility of the process. (b) For a system composed of the pound of air that was originally at 70 psia, calculate the same quantities. (c) For the system composed of the pound of air originally



at 15 psia, calculate the same quantities. (d) Compare your answers to parts *b* and *c* with your answer to part *a*, and explain any apparent inconsistency.

13. Plot a *bs* chart for steam. Show (a) the saturated-liquid and saturated-vapor lines and the critical point, (b) lines of constant pressure of 4000, 2000, and 14.7 psia and 0.25 in. Hg abs, (c) lines of constant temperature of 800, 600, 60, and 32°F, and (d) the triple-point region.

14. Show the appearance of a steady-flow Rankine cycle based on 1 lb of H<sub>2</sub>O on the chart of Prob. 13. Assume that  $p_u = 200$  psia,  $p_1 = 14.7$  psia, and (a) that the steam is saturated as it enters the prime mover and (b) that its temperature is 500°F at this point in the cycle.

15. Work Example 16:5A, changing the temperature of the atmosphere to 60°F. Compare with results of the example as solved in the text, and state your conclusions.

16. Work Example 16:5A, changing the original state of the H<sub>2</sub>O to a saturated vapor at 100 psia and the temperature of the atmosphere to 60°F.

17. A steady stream of air at 2 psia and 60°F enters a process at negligible velocity. What is its availability per pound? During the process, it expands adiabatically and reversibly to a pressure of 1 psia. At what velocity does it leave the process? Calculate the change of availability per pound. Show that the irreversibility of the process is zero.

18. A steady stream of H<sub>2</sub>O enters a process at 100 psia, 400°F, and at a velocity of 100 fps. Calculate the change of availability and the irreversibility, per pound of H<sub>2</sub>O, for each of the following processes: (a) The stream is heated slowly at constant pressure until its temperature is 500°F. The passage has a constant cross-sectional area and is horizontal. (b) As it passes through a horizontal pipe of constant diameter, it is heated to 500°F. Because of friction, the final pressure is 90 psia. (c) It expands adiabatically and reversibly through a nozzle to a pressure of 14.7 psia. (d) It expands adiabatically through a nozzle which it leaves at 14.7 psia and a quality of 0.95. (e) It is throttled slowly and adiabatically to a pressure of 14.7 psia. The velocity at exit differs negligibly from the initial velocity. (f) It expands adiabatically to 14.7 psia as it passes through a turbine with an efficiency of 55 per cent.

19. The stream of air described in Prob. 17 enters a compressor which raises its pressure to 14.7 psia. It leaves the compressor at a velocity of 100 fps. Calculate the change of availability per pound in the compressor and the irreversibility of the compressor process, based on the following assumptions: (a) The compression is adiabatic and reversible. (b) The compression is isothermal and reversible. (c) The final temperature of the air is 600°F, and the compression is adiabatic. (d) The compression is adiabatic, and the compressor has an adiabatic efficiency of 80 per cent.

20. In Prob. 19, let the air enter the compressor at 14.7 psia and 60°F at negligible velocity. It leaves at 100 psia, also at negligible velocity. Calculate the change of availability and the irreversibility of the process, per pound of air, for each of the processes described in parts *a* to *d* of Prob. 19.

21. In Example 16:5B, assume the temperature of the atmosphere to be 60°F, and calculate the same quantities. Compare with the answers of the example, and state your conclusions.

22. In Example 16:5B, let  $p_0 = 14.7$  psia and  $t_0 = 70^\circ\text{F}$  as in the example, but assume that the steam is expanded to a final pressure of 1 psia. Compare your answers with those of the example, and state your conclusions.

23. A steady stream of exhaust steam enters a surface condenser at 1 psia and a quality of 0.95 at negligible velocity. It leaves as a saturated liquid at the same pressure and at negligible velocity as the result of an energy transfer with a steady stream of cooling water which enters at 60°F and leaves at 80°F. (a) Calculate the



weight of cooling water circulated per pound of steam condensed. (b) Considering 1 lb of condensing steam as the system, what is the change of availability and the irreversibility that accompany the process? (c) What are the similar quantities when the system is the weight of cooling water that is required to condense 1 lb of steam? (d) For a system composed of 1 lb of condensing steam plus the weight of cooling water that must be circulated to bring about its condensation, what are the change of availability and the irreversibility of the process? (e) Compare the answers to (b) and (c) with the answer to part d, and explain any apparent discrepancy.

24. In Example 14:4, 0.119 lb of steam at 225 psia and a specific enthalpy of 1123 Btu enters the high-pressure regenerative feedwater heater and is condensed to a saturated liquid at the same pressure while 0.881 lb of feedwater at 600 psia and 294.8°F ( $h = 264.3$ ) enters from the second heater and is raised at constant pressure to a temperature of 391.8°F ( $h = 366.1$ ). What is the irreversibility of the process that takes place in this heater? Assume velocities to be negligible.

25. In Example 14:4, calculate the irreversibility of the processes that take place in (a) the intermediate heater and (b) the low-pressure heater, per pound of steam supplied the turbine by the boiler.

26. In a steam power plant that operates condensing at an exhaust pressure of 2 psia, a part of the steam is used to supply steam-driven auxiliaries such as the feedwater pump, blowers, etc. The exhaust from these auxiliaries is available at atmospheric pressure and can be used to preheat the feedwater in an open feedwater heater, in which it mixes directly with the feedwater. The exhaust steam is saturated as it enters the heater; the feedwater enters at 100°F, and the mixture of feedwater and condensate leaves at 210°F. Per pound of feedwater entering the boiler, *i.e.*, per pound of the mixture, calculate the irreversibility of the process.

27. A throttling governor throttles the saturated steam leaving the boiler at a pressure of 150 psia to a pressure of 100 psia before it enters the prime mover. Per pound of steam, calculate the irreversibility of the process carried out by the governor.

28. In an economizer, the flue gases ( $c_p = 0.24$ ) are used to preheat the feedwater entering the boiler of a steam power plant and, in doing so, decrease in temperature from 630 to 400°F. The feedwater is heated from 210 to 290°F. Find, per pound of feedwater entering the boiler, (a) the weight of flue gas cooled and (b) the change of availability and the irreversibility of the process carried out in the economizer.

29. In an air preheater, the ratio of the mass rate of flow of flue gas ( $c_p = 0.24$ ) to that of the air for combustion is 1.05. Fourteen pounds of air is supplied for the combustion of each pound of coal fired, and 10 lb of steam is generated per pound of coal. The air for combustion is heated from 60 to 210°F. The flue gas enters the preheater at 580°F. Per pound of steam generated, what are the change of availability and the irreversibility of the process that takes place in the air preheater?

30. In Example 11:14, calculate the effectiveness of each of the four stages. What data must be introduced other than those included in the statement of the example?

31. Use the data of Example 11:14, but assume equal stage effectivenesses of 70 per cent. (a) Calculate the efficiency of each stage and the efficiency of the turbine. (b) Calculate the effectiveness of the complete turbine. (c) Show that the condition curve is a straight line.

32. Use the data of Example 11:14, but assume stage effectiveness to be as follows: first stage, 80 per cent; second stage, 75 per cent; third stage, 70 per cent; fourth stage, 65 per cent. (a) What is the condition of the steam as it leaves the turbine (neglect velocity)? (b) Calculate the efficiency of each stage and of the turbine. (c) Calculate the effectiveness of the turbine, and show that it equals an average of the effectivenesses of the individual stages when that average is weighted according to the respective decreases in  $b$  in the stages.



33. (a) Prove the statement made in the text to the effect that if the effectiveness of each stage of a turbine is the same, the over-all effectiveness of the turbine will be identical with that of each of its stages. (b) Prove that the condition line is a straight line for a turbine having stages of equal effectiveness. (c) Prove that the effectiveness of a turbine is an average of the effectivenesses of its stages when that average is weighted according to the decrease in availability in each stage.

34. (a) A turbine stage receives steam at 400 psia, 600°F, and exhausts at 200 psia. Its effectiveness is 72 per cent. Calculate the enthalpy drop, the decrease of availability, the efficiency, and the irreversibility per pound of steam in this stage. Neglect velocities.

(b) The last stage of this turbine exhausts wet steam at a pressure of 1 in. Hg abs and a quality of 0.85. The isentropic enthalpy drop for this stage is the same as for the stage described in part *a*, and its effectiveness is also 72 per cent. What is the condition of the steam as it enters the last stage? What is the actual enthalpy drop in this stage? What are the decrease of availability and the irreversibility per pound of steam in this stage? What is the stage efficiency? Neglect velocities.

### Symbols

$b$	$h - T_0s$ , a part of the availability function of unit mass in steady flow
$c_p$	specific heat at constant pressure
$e$	stored energy of a system of unit mass
$E$	stored energy of a system
$g$	acceleration of gravity
$h$	specific enthalpy
$J$	proportionality factor
$M$	mass rate of flow
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$P_0$	pressure of the atmosphere
$Q$	heat flow; rate of heat flow
$s$	specific entropy
$S$	entropy of a system
$T$	absolute temperature
$T_0$	absolute temperature of the atmosphere
$u$	specific internal energy
$v$	specific volume
$V$	volume of a system
$\bar{V}$	velocity
$W$	work; rate of work delivery
$x$	quality of a vapor
$z$	elevation

### Greek Letters

$\beta$	availability function of a simple system of unit mass
$\epsilon_s$	effectiveness of a turbine stage
$\eta_s$	efficiency of a turbine stage

### Subscripts

0	at the dead state
$s$	stage
$u$	useful

## CHAPTER 17

### THE STEADY FLOW OF FLUIDS IN PIPES AND DUCTS

**17:1. Introduction.** In Chap. 11, in discussing the flow of fluids through nozzles, the basic assumption was made that the flow was adiabatic and reversible. Although this assumption was never quite justified, the deviations from reversibility in flow were relatively small and could be conveniently expressed in terms of so-called “velocity” and “discharge” coefficients having values usually very close to 1.

If we apply the assumption that the flow is reversible as well as adiabatic to the flow of a fluid through a channel of constant cross-sectional area, such as a pipe, the following flow conditions would follow:

1. The state of the fluid, including its velocity, would be identical at all points along the passage.

2. Since there is no differential of pressure, no power would be required to transport the fluid through a channel of any length.

3. The mass rate of fluid flow would depend only on its specific volume and its velocity, both of which would be the same at all sections of the channel, and therefore would be independent of the length of the channel.

The conditions for the adiabatic flow of real fluids through long pipes and ducts are readily recognized as bearing no resemblance to those outlined above. The pressure will decrease in the direction of flow, often with an increase in specific volume and velocity as a consequence, power will be required for the transport of the real fluid, and the mass rate of flow will depend on the differential of pressure that is maintained between entrance and exit and upon the length of the passage. The cause of the irreversibility is found in the property of the real fluid that is called *viscosity*. Because of its viscosity, the fluid tends to be slowed by its contact with the walls of the channel. But the same mass rate of flow must be maintained past each channel section, just as in flow through a nozzle, and a decrease of pressure in the direction of flow becomes necessary to maintain the required velocity. In the case of compressible fluids, this pressure differential is still further increased by the increase in specific volume that accompanies reduced pressure, making it necessary that the velocity be not just maintained at the same value for successive sections but increased in proportion to the increase in specific volume.

The force applied by the walls of the channel on the column of fluid, due to the latter's viscosity, can act only to decrease the velocity of the



fluid relative to these walls; the action of viscosity is thus to create an irreversibility. It is only because of the relatively short length of a nozzle that the flow through it may be assumed to approach reversibility.

There have been many occasions in earlier chapters when reference, direct or implied, was made to the viscosity of the real fluid. For example, the paddle-wheel process first discussed in Art. 1:7 was a possible means of introducing energy into the system only because that system was composed of a real fluid with viscosity as one of its properties. Previous references have, however, been of a general character, and no attempt has been made to measure the forces that are set up as the result of viscosity. Since viscosity is an important property in connection with the flow of real fluids through long pipes and ducts, that discussion can no longer be delayed.

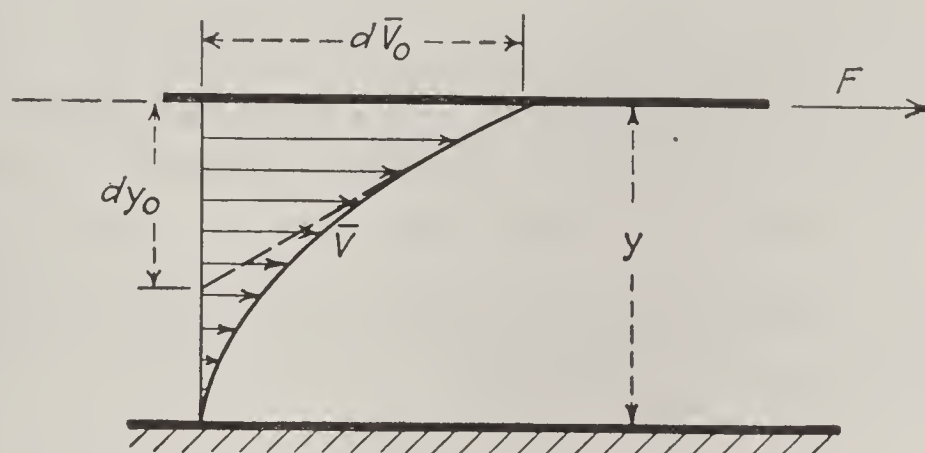


FIG. 17:1. Viscosity and velocity gradient.

**17:2. Viscosity and Viscous Drag.** Viscosity is the resistance that the fluid offers to shearing motion. Consider, as in Fig. 17:1, two parallel flat plates separated by a slice of fluid having the thickness  $y$ . The lower plate is anchored and remains stationary; the upper plate, of area  $A$ , is kept in slow motion at a velocity  $\bar{V}$  through the agency of a force  $F$  which acts in the plane of the plate; the magnitude of this force is a measure of the *viscous drag*.

Experiment has shown that a thin layer of the fluid will remain attached to each plate, the layer attached to the lower plate thus being stationary and that attached to the upper having the velocity  $\bar{V}$ . Intervening laminae of fluid will move with intermediate velocities which will be greater as their distance from the lower plate increases. If the velocity is slow, the particles of fluid in these laminae will follow nonintersecting (*streamline*) paths, and the motion of the fluid may be described as *laminar* or *streamline*, or since the force exerted by a lamination in slowing or accelerating more or less rapidly traveling adjacent laminae is due solely to the effects of viscosity, the term *viscous flow* is also used. When the velocity exceeds a certain critical value which will be shown later to depend on the distance between the plates and the density and viscosity

of the fluid, particles will begin to cross paths and to collide with each other; the flow is now beginning to be *turbulent*. In the present article we shall confine ourselves to a discussion of laminar flow; a discussion of the effects produced in turbulent flow will be taken up later.

In Fig. 17:1 is shown a velocity profile that plots the velocity of each fluid lamination with respect to its position between the two plates; in general, unless the distance between the plates is very small, this will be a curve as shown. The slope  $d\bar{V}/dy$  of this curve is therefore not constant. Experiment has shown that the force  $F$  will be in proportion to the slope of this curve in the laminations immediately adjacent to the plate to which the force is applied, *i.e.*, to the ratio  $(d\bar{V}/dy)_0$  shown in the figure; this is called the *velocity gradient*. The force  $F$  will also depend on the area  $A$  of the upper plate. This area is the “wetted” surface; if the plate is submerged, the area of both sides must be considered, each, of course, being used in conjunction with its respective value of  $(d\bar{V}/dy)_0$ . Another factor in the size of  $F$  is the viscosity of the fluid, which will be designated as  $\mu$ . It is the arbitrary practice to assign a value to  $\mu$  which is in direct proportion to  $F$  under equivalent conditions as to area and velocity gradient. These are the only factors that control the size of  $F$  in laminar flow, and we may write an expression for the resistance  $R$  (force per unit area of wetted surface) in the form

$$R = \frac{F}{A} = \mu \left( \frac{d\bar{V}}{dy} \right)_0 \quad (17:1)$$

in which  $\mu$  is a dimensional constant that expresses the relative viscosity and is called the *coefficient of viscosity* of the fluid. Since the coefficient of viscosity is not dimensionless, as an examination of Eq. (17:1) will show, the value it has in expressing a given viscosity will vary with the units in which  $F$ ,  $A$ ,  $\bar{V}$ , and  $y$  are measured. When the unit of force is the dyne, of distance is the centimeter, and of time is the second, the corresponding unit of viscosity is called the *poise*. It has become usual practice to express the viscosity in tables, equations, and charts in terms of the centipoise, or  $\frac{1}{100}$  poise.

In general, the viscosity of a fluid is practically independent of its pressure<sup>1</sup> and is primarily a function of its temperature. If the fluid is a liquid, its viscosity will decrease with increased temperature; if a gas, increased viscosity will accompany increased temperature. Table 17:1 gives approximate equations for the viscosity, in centipoises, of a few gases and liquids. These equations are valid only in the approximate

<sup>1</sup> This is true except for a vapor at a temperature that is close to its boiling point. For a few vapors (see, for example, Keenan and Keyes, “Thermodynamic Properties of Steam,” Table 6, p. 76, John Wiley & Sons, Inc., New York, 1936) the effect of pressure on viscosity has been investigated.



range 0 to 200°F. They show a straight-line relation between viscosity and temperature; the actual relation is not nearly so simple, but these equations are presented for the convenience of the reader in the solution of problems to follow and to illustrate the typical manner in which viscosity increases with increase of gas temperature, or decrease of liquid temperature.

TABLE 17:1. VISCOSITY OF GASES AND LIQUIDS  
t in °F, viscosity in centipoises

Substance	Equation	Substance	Equation
Gases		Liquids	
Air.....	$\mu = 0.0165 + 2.5 \times 10^{-5}t$	Gasoline, sp. gr = 0.7.	$\mu = 0.57 - 0.0021t$
Oxygen.....	$\mu = 0.018 + 2.5 \times 10^{-5}t$	Lubricating oils	
Nitrogen.....	$\mu = 0.0155 + 2.5 \times 10^{-5}t$	SAE 10.....	$\mu = 160 - t$
Hydrogen.....	$\mu = 0.0078 + 1.25 \times 10^{-5}t$	SAE 30.....	$\mu = 649 - 4.15t$
Carbon dioxide.....	$\mu = 0.0133 + 2.5 \times 10^{-5}t$	Mercury.....	$\mu = 1.80 - 0.003t$
Steam.....	$\mu = 0.0083 + 2 \times 10^{-5}t$	Water	
Methane.....	$\mu = 0.0095 + 1.5 \times 10^{-5}t$	32-100°F.....	$\mu = 2.317 - 0.0164t$
		100-212°F.....	$\mu = 1.027 - 0.0035t$

Viscosity is a property of the fluid. Thus, although the value given  $\mu$  is based on the resistance to laminar flow, this value will also describe the viscosity of the same fluid at the same state, even when the flow is turbulent.

The equation presented in Table 17:1 for the calculation of the viscosity of steam applies only at low pressure. A much more complete and accurate picture in respect to the viscosity of steam and of water is found in Table 6 of the Keenan and Keyes steam tables. In Table 6, the unit of viscosity is based on the pound of force, the second, and the foot (lb-sec/ft<sup>2</sup>). This unit of viscosity corresponds to 47,800 centipoises.

**17:3. Dimensional Analysis.** Even when the value of  $\mu$ , the coefficient of viscosity, is known, Eq. (17:1) offers little direct assistance to the engineer in the calculation of the effect of fluid viscosity on the flow through a long pipe or duct. Before the magnitude of the force that acts to slow the column of fluid may be computed, he must be able to assign a value to the velocity gradient if that equation is used, and that velocity gradient is affected by a number of factors such as the density of the fluid, the average velocity of flow in the channel, and the size (diameter) of the pipe as well as the viscosity of the fluid. Moreover, as has been stated, Eq. (17:1) is valid only for low velocities. In order to express the way in which the various factors interact and to determine their combined effect on the resistance to flow, the engineer uses a tool which he calls *dimensional analysis*.

The basic dimensions with which the engineer is concerned include mass

( $M$ ), length, or distance ( $L$ ), and time ( $\theta$ ).<sup>1</sup> There are many units of mass with which the engineer deals; the pound, the slug, and the gram are examples. We may write

$$1 \text{ slug} = 32.2 \text{ lb mass}$$

This equation is based on the definition of the pound mass as that mass which *weighs* one pound if placed in the earth's gravitational field. On the other hand, it would be dimensionally incorrect to write the preceding relation as "1 slug = 32.2 lb *weight*," for it is only in a gravitational field of an intensity equal to that of the earth's that 1 slug would *weigh* 32.2 lb.

A large number of quantities, such as force, weight, mass, velocity, elevation, acceleration, moment, work, heat, energy, etc., enter into engineering calculations, and there are various units in which the amounts of each may be measured. But each of these quantities may be expressed in terms of the basic dimensions  $M$ ,  $L$ , and  $\theta$  without regard to the units in terms of which its measurement is to be made. Thus, to list only the few on which our interest is, for the moment, centered:

$$\begin{aligned} \text{Mass} &= [M] \\ \text{Length} &= [L] \\ \text{Time} &= [\theta] \\ \text{Area } [A] &= [L^2] \\ \text{Volume } [V] &= [L^3] \\ \text{Mass density } [\rho] &= \left[ \frac{M}{L^3} \right] \\ \text{Velocity } [\bar{V}] &= \left[ \frac{L}{\theta} \right] \\ \text{Acceleration } \left[ \frac{d\bar{V}}{d\theta} \right] &= \left[ \frac{L}{\theta^2} \right] \\ \text{Force (mass} \times \text{acceleration)} [F] &= \left[ \frac{ML}{\theta^2} \right] \end{aligned}$$

In each of the foregoing expressions, the brackets are used to identify the equality as being one of dimensions rather than, necessarily, of units of measurement. For example, the dimensional expression for velocity above may be read as "The dimension of velocity is equal to the dimension of length divided by the dimension of time." We shall add one more to this short list as being necessary to our present purpose. To express the viscosity dimensionally, we note from Eq. (17:1) that

<sup>1</sup> Force ( $F$ ), length ( $L$ ), and time ( $\theta$ ) may also be used. In that case, the dimensions of mass would be expressed in terms of the dimensions of force, length, and time. It is sometimes convenient to add a temperature dimension ( $T$ ).



$$\mu = \frac{F dy}{A d\bar{V}}$$

or

$$[\mu] = \left[ \frac{ML}{\theta^2} \right] [L] \left[ \frac{1}{L^2} \right] \left[ \frac{\theta}{L} \right] = \left[ \frac{M}{L\theta} \right]$$

To be correct, an engineering equation must be dimensionally consistent, *i.e.*, the dimensions on the two sides of the equality sign must agree. This principle is often used to check the correctness of an equation; conversely, it may be used to set up a relation that is dimensionally correct. In this case it is our desire to formulate an equation which will express the resistance offered to the flow of a fluid through a pipe or conduit. This expression, to be accurate and usable, should reflect the effects of the various factors which our analysis of the situation has indicated will affect the amount of this drag. These factors, as they have been listed above, include the mass density of the fluid, its viscosity, its velocity of flow in the channel, and the size of the channel. Thus we may write

$$R = \frac{F}{A} = f(\rho, \mu, \bar{V}, D) \quad (1)$$

in which  $R$  is the resistance to flow per unit area of contact with the flowing fluid (per unit area of wall surface),  $\rho$  is the mass density of the fluid,  $\mu$  is its viscosity and  $\bar{V}$  its velocity, and  $D$  is a dimension of the channel, conventionally the diameter if the channel is round in cross section.

The degree to which each of the quantities  $\rho$ ,  $\mu$ ,  $\bar{V}$ , and  $D$  individually affects the resistance to flow is unknown but may be expressed by assigning to each an unknown exponent. Thus (1) may be written in the form

$$R = C\rho^a\mu^b\bar{V}^cD^d \quad (2)$$

in which  $C$  is a dimensionless constant of proportionality and  $a$ ,  $b$ ,  $c$ , and  $d$  are the exponents expressing the unknown parts which the quantities to which they are respectively attached play in accounting for the resistance to flow. This equation may be written dimensionally in the form

$$[R] = \left[ \frac{F}{A} \right] = \left[ \frac{ML}{\theta^2} \right] \left[ \frac{1}{L^2} \right] = \left[ \frac{M}{L\theta^2} \right] = \left[ \frac{M}{L^3} \right]^a \left[ \frac{M}{L\theta} \right]^b \left[ \frac{L}{\theta} \right]^c [L]^d \quad (3)$$

Noting that the dimensions must be consistent, we may write

$$\begin{aligned} \text{Based on the mass dimension:} & \quad a + b = 1 \\ \text{Based on the length dimension:} & \quad -3a - b + c + d = -1 \\ \text{Based on the time dimension:} & \quad -b - c = -2 \end{aligned} \quad (4)$$

There are thus three equations and four unknowns ( $a, b, c, d$ ) so that, in solving, values of the unknowns must be expressed in terms of one of their

number. Observing that  $b$  is the only term that appears in every one of the group (4) equations, it is selected for this use, and we obtain

$$\begin{aligned} a &= 1 - b \\ c &= 2 - b \\ d &= 3(1 - b) + b - (2 - b) - 1 = -b \end{aligned} \quad (5)$$

These values may be substituted in (2), giving

$$R = C\rho^{1-b}\mu^b\bar{V}^{2-b}D^{-b} = C\rho\bar{V}^2\left(\frac{\rho\bar{V}D}{\mu}\right)^{-b} \quad (6)$$

A test will show that the product  $\rho\bar{V}D/\mu$  is dimensionless; it is known as the *Reynolds number*. Since it is dimensionless it may be combined with the dimensionless constant  $C$  to give a *coefficient of friction*  $\mathbf{f}$ ,

$$\mathbf{f} = C\left(\frac{\rho\bar{V}D}{\mu}\right)^{-b} \quad (17:2)$$

indicating that this coefficient of friction, though dimensionless, is not constant but is some unknown function of the Reynolds number. Returning to (6), we may write

$$R = \mathbf{f}\rho\bar{V}^2 \quad (17:3)$$

Dimensional analysis carries no further than to this point. To determine what relation exists between  $\mathbf{f}$  and  $\text{Re}$ , the Reynolds number, we must resort to experiment. Moreover, the results of dimensional analysis can be no more accurate than has been our analysis of the factors that affect the desired quantity. For instance, in the above example of dimensional analysis the factors chosen were four in number, while the number of dimensions was three; this produced a single dimensionless number on which the coefficient of friction will depend. But, in Chap. 11, it is indicated that the velocity of sound is also a factor in the high-speed flow of gases and vapors. If the velocity of sound,  $\bar{V}_s$ , had been included, the number of unknowns in the group (4) equations would have been five and two dimensionless quantities, instead of one, would have resulted. It may be shown that one of the two would have been the Reynolds number, the other the ratio of fluid velocity to the velocity of sound in the fluid, or  $\bar{V}/\bar{V}_s$ . This is the *Mach number*, a ratio of considerable importance in studying the flow of gases or vapors at velocities close to the velocity of sound. At low Mach number the influence of Reynolds number is predominant; it is the Reynolds number that is of principal importance in the study of fluid flow through pipes and ducts.

*Example 17:3.* Add the velocity of sound in the fluid to the factors assumed in Art. 17:3 to affect the resistance to flow. Show that the coefficient of friction will in that case depend on the Mach number as well as the Reynolds number.



Solution:

$$R = f(\rho, \mu, \bar{V}, D, \bar{V}_s)$$

or

$$R = C\rho^a\mu^b\bar{V}^cD^d\bar{V}_s^e$$
$$\left[\frac{M}{L\theta^2}\right] = \left[\frac{M}{L^3}\right]^a\left[\frac{M}{L\theta}\right]^b\left[\frac{L}{\theta}\right]^c[L]^d\left[\frac{L}{\theta}\right]^e$$

Based on the mass dimension:  $a + b = 1$

Based on the length dimension:  $-3a - b + c + d + e = -1$

Based on the time dimension:  $-b - c - e = -2$

or

$$a = 1 - b$$
$$c = 2 - b - e$$
$$d = -b$$

and

$$R = C\rho^{1-b}\mu^b\bar{V}^{2-b-e}D^{-b}\bar{V}_s^e = C\rho\bar{V}^2\left(\frac{\rho\bar{V}D}{\mu}\right)^{-b}\left(\frac{\bar{V}}{\bar{V}_s}\right)^{-e}$$

Therefore

$$R = f\rho\bar{V}^2$$

where  $f$  is a function of both the Reynolds number and the Mach number.

**17:4. Effect of Reynolds Number on Flow Characteristics.** Equation (17:1) is based on the assumption that the flow in the pipe or duct is *laminar*, i.e., that the particles of fluid follow straight paths parallel with the axis of the channel, with the greatest velocity at this axis and zero velocity for a thin layer immediately adjacent to the wall of the passage; this, it will be remembered, is also called viscous, or streamline, flow. The equation indicates that, for this type of flow, the resistance  $R$  is proportional to the velocity gradient  $(d\bar{V}/dy)_0$ . Experiment has shown that laminar flow is found only at low values of the Reynolds number. As the Reynolds number increases above a certain critical value, which depends on factors such as the roughness of the wall surface and the straightness of the channel, the flow becomes turbulent. In turbulent flow, the particles of fluid acquire a radial component of velocity, and eddies are formed. Particles of fluid from the inner laminae of flow begin to mix with the less rapidly traveling particles nearer the walls of the channel and, because of their higher velocity, increase the velocity of flow near the edges of the stream.

As might be expected, the transition from laminar to turbulent flow is not abrupt but occurs gradually. As the velocity of flow increases, the point is reached where the more rapidly traveling elements near the axis of the channel begin to acquire a turbulent motion. As these particles, due to the radial component of velocity they have now added, mix with the particles of fluid in adjacent laminae, they give turbulence to a wider section of the flow. Turbulence spreads in this manner, as the velocity

of flow further increases, until the entire flow, with the exception of a very thin stationary layer at the wall of the duct, becomes turbulent. This interval during which turbulence is spreading is called the *transition* period. After the flow has become fully turbulent, the resistance varies more nearly in proportion to the square of fluid velocity than to its first power, as in laminar flow.

In laminar flow the distribution of velocity across the pipe is parabolic, varying from a maximum at the axis of flow to zero at the walls; the velocity profile is shown as curve 1 of Fig. 17:2. Curves 2 and 3 of that figure show the idealized velocity profiles during the transition period and when full turbulence has been attained, respectively.

When the velocity profile is parabolic, as in laminar flow, it may be shown that the average velocity of the fluid is one-half the maximum

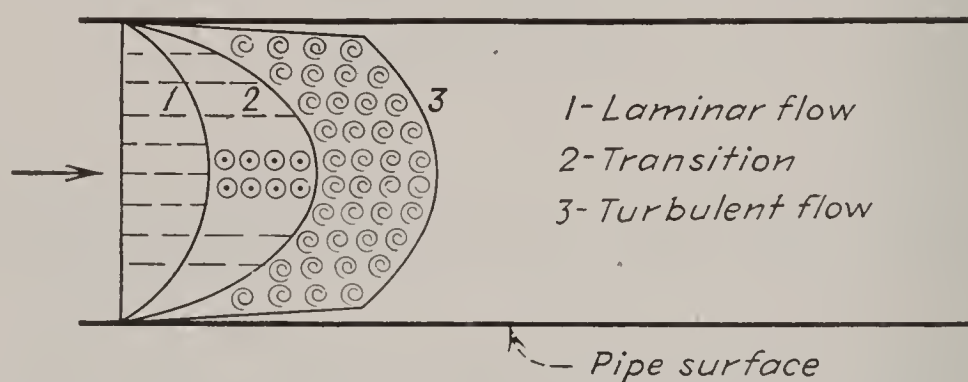


FIG. 17:2. Velocity profiles—laminar to turbulent flow.

velocity at the axis of the pipe. As turbulence begins to make its appearance, that ratio increases rapidly, as may be judged from comparison of the velocity profiles of Fig. 17:2, reaching a value of about 0.8 as full turbulence is attained. Further increase of fluid velocity still further increases the ratio until, for velocities of the order of those existing in nozzles, it becomes very nearly 1.

The mass rate of flow through a pipe or duct is, of course, based on the average velocity of the fluid; in expressing the kinetic-energy term of Eq. (3:5), the average velocity would therefore be used. Since the kinetic energy varies with the square of the velocity, this introduces an error into its calculation; it may be shown that the kinetic energy for laminar flow in a pipe is  $\bar{V}_{av}^2/g$  per pound and thus is twice the value as based on the assumption of a uniform velocity. However, as will be shown later, laminar flow occurs only at very low velocities, and the error is small in amount as compared with other terms of Eq. (3:5). When, as in nozzle flow, the kinetic-energy term is of major importance, we find that  $\bar{V}_{av}$  is very nearly equal to  $\bar{V}_{max}$  and the error in assuming a uniform velocity in the calculation of the kinetic energy is again small.

As has been stated above, the point at which the flow begins to lose its laminar character will depend upon factors such as the roughness of the wall surface and the straightness of the passage. The critical Re varies



from about 1200 to around 2000. Fully turbulent flow may be reached at Reynolds numbers in the usual range of 2500 to 4000. Even the upper value of 2000 for the critical Reynolds number is very low; it throws nearly all of the flows with which the engineer is concerned in practice into the range of full turbulence. For example, in the flow of water at 100°F through a 1-in. pipe, it corresponds to a velocity of about 0.17 fps; in the flow of air at 14.7 psia, 70°F, through a round duct of 1 ft diameter, it is equivalent to a velocity of approximately 0.33 fps. The chief interest of the engineer in the resistance to fluid flow is centered in the pressure drop that must be maintained to balance it and in the power requirement that results from that pressure drop; at velocities of this order, pressure drops would be so small as, in his estimation, to be negligible. One of the fields of engineering interest in which laminar flow may be of importance is found in situations where the pressure to propel the fluid must be furnished by convective effects, *i.e.*, by differences in density of the fluid itself; here the available heads, and thus the velocities, are low. An example is the gravity-flow hot-water heating system.

The resistance in laminar flow is proportional to the first power of the velocity. Therefore, if Eq. (17:3) is to be used to calculate the resistance, the friction coefficient  $f$  should vary inversely with the velocity, *i.e.*, inversely with the Reynolds number in the flow of the same fluid through the same pipe. Experiment has shown that, for laminar flow in pipes and ducts,

$$f = \frac{8}{\text{Re}} \quad (17:4)$$

and that this value is independent of a reasonable variation in the roughness of the pipe surface.

For fully turbulent flow in smooth tubes, various experimentally determined expressions for  $f$  are available, all of which give its value in terms of the Reynolds number and all of which are in fairly close agreement. We shall arbitrarily select from these the relation

$$f = 0.0395(\text{Re})^{-1/4} \quad (17:5)$$

\* This is the Blasius relation and is selected because of its simplicity. A formula of more general acceptance is the Nikuradse equation:

$$f = 0.0004 + 0.0276(\text{Re})^{-0.237}$$

This equation also applies to turbulent flow in smooth tubes. For commercial pipe in small sizes (about 1 in.), values of  $f$  are about 30 per cent higher than as obtained from the Nikuradse equation. The percentage addition that is made to  $f$  as obtained from either the Blasius or the Nikuradse equation is based on the relative roughness. This is expressed in terms of a *roughness factor*, defined as the ratio of the radius of the pipe to the depth of the surface projection. The percentage increase in  $f$  will be less for higher values of the roughness factor and is thus less for the larger sizes of commercial pipe.

as applying to turbulent flow in smooth tubes. The resistance to turbulent flow is considerably increased by roughness of the wall surface, and the use of Eq. (17:5) is correspondingly limited, but it will serve our purposes in thermodynamic analysis. Equation (17:5), in conjunction with Eq. (17:3), shows a variation of resistance in proportion to somewhat less than the second power of the velocity.

In Fig. 17:3, Eq. (17:4) is plotted in the range of Reynolds numbers that is associated with laminar flow, and Eq. (17:5) is used to show the variation of the friction coefficient with Reynolds number in the earlier phases of turbulent flow. Since the chief purpose of this figure is to show

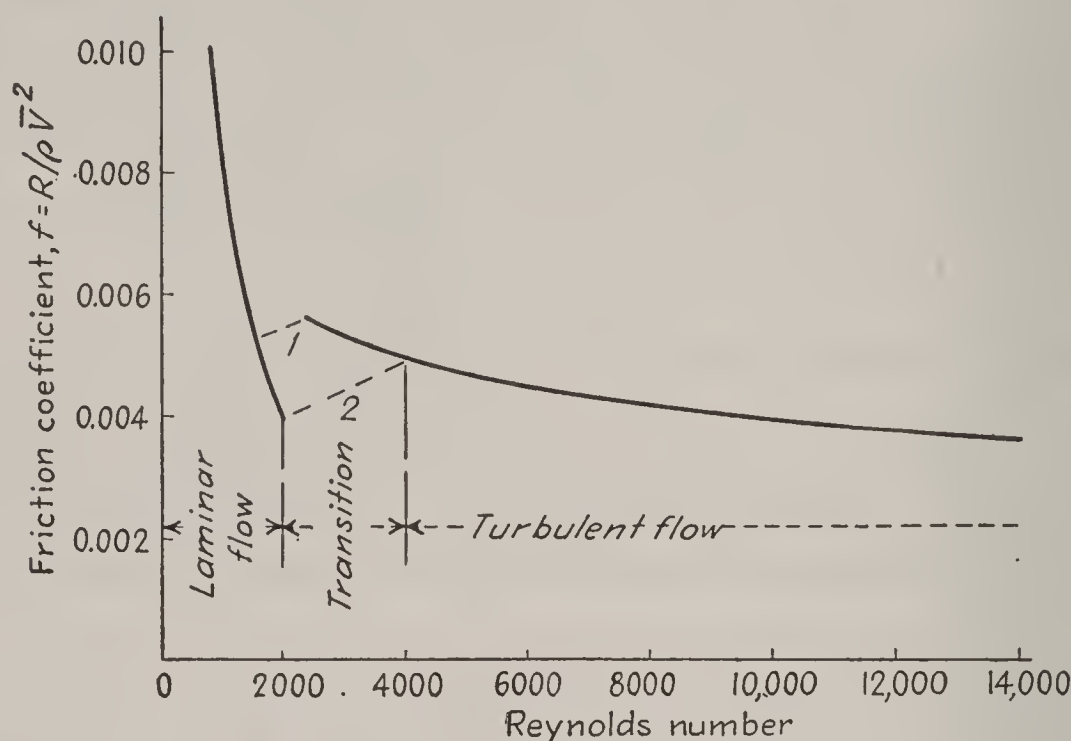


FIG. 17:3. Variation of friction coefficient at low Reynolds number—smooth tubes.

the transition between laminar and turbulent flow, only the lower Reynolds numbers are included. Two transition curves are shown by the lines numbered 1 and 2; curve 1 assumes that the critical Re is about 1200 and that the flow is fully turbulent at  $Re = 2500$ , while curve 2 places these points at  $Re = 2000$  and  $Re = 4000$ , respectively. The curves are dashed to indicate that the value of the friction coefficient is somewhat unpredictable in this transition period; experiment has indicated that it will depend on whether the velocity (the Reynolds number) is increasing or decreasing at the moment. In fact, it may be found that the transition will be similar to that shown as curve 2 if velocities are gradually increased, while, for decreasing velocities, the return to laminar flow will approximate curve 1.

*Example 17:4A.* Assuming the critical value of the Reynolds number to be 2000, calculate the highest average velocity for laminar flow when (a) water at  $100^{\circ}\text{F}$  flows through a 1-in. pipe and (b) air at 14.7 psia,  $70^{\circ}\text{F}$ , flows through a round duct of 1 ft diameter. What is the maximum velocity in each case?



*Solution:*

(a) The inside diameter of a 1-in. pipe is 1.05 in.

$$\rho = \frac{62.0}{32.2} = 1.93 \text{ lb-sec}^2/\text{ft}^4$$

$$\mu = 2.317 - (0.0164)(100) = 0.677 \text{ centipoise}$$

$$\text{Re} = 2000 = \frac{\bar{V} D \rho}{\mu} = \bar{V} \left( \frac{1.05}{12} \right) (1.93) \left( \frac{47,800}{0.677} \right)$$

or

$$\bar{V}_{\text{av}} = 0.168 \text{ fps}$$

$$\bar{V}_{\text{max}} = 2\bar{V}_{\text{av}} = 0.336 \text{ fps}$$

$$(b) \rho = \frac{1}{g\nu} = \frac{P}{gRT} = \frac{(14.7)(144)}{(32.2)(53.3)(530)} = 0.00232 \text{ lb-sec}^2/\text{ft}^4$$

$$\mu = 0.0165 + (2.5 \times 10^{-5})(70) = 0.0183 \text{ centipoise}$$

$$\text{Re} = 2000 = \frac{\bar{V} D \rho}{\mu} = \frac{\bar{V}(1)(0.00232)(47,800)}{0.0183}$$

or,

$$\bar{V}_{\text{av}} = 0.33 \text{ fps}$$

$$\bar{V}_{\text{max}} = 2\bar{V}_{\text{av}} = 0.66 \text{ fps}$$

*Example 17:4B.* Calculate the resistance corresponding to the conditions of parts *a* and *b* of Example 17:4A.

*Solution:*

$$(a) f = \frac{8}{2000} = 0.004; R = f\rho\bar{V}^2 = (0.004)(1.93)(0.168)^2 = 0.000218 \text{ fps}$$

$$(b) f = 0.004; R = (0.004)(0.00232)(0.33)^2 = 0.00000101 \text{ psf.}$$

*Example 17:4C.* Find the resistance and the maximum velocity when the average velocity is 30 fps in the flow of (a) water at 100°F through a smooth tube of 1 in. inside diameter and (b) air at 14.7 psia, 70°F, through a smooth duct of 1 ft inside diameter.

*Solution:*

$$(a) \text{Re} = \frac{(30)(1)(1.93)(47,800)}{(12)(0.677)} = 340,000$$

This is turbulent flow, and Eq. (17:5) applies

$$f = (0.0395)(340,000)^{-1/4} = \frac{0.0395}{24.1} = 0.00164$$

$$R = f\rho\bar{V}^2 = (0.00164)(1.93)(30)^2 = 2.84 \text{ psf}$$

$$\bar{V}_{\text{max}} = \frac{\bar{V}_{\text{av}}}{0.8} = \frac{30}{0.8} = 37.5 \text{ fps}$$

$$(b) \text{Re} = \frac{(30)(1)(0.00232)(47,800)}{0.0183} = 182,000 \text{ (turbulent flow)}$$

$$f = (0.0395)(182,000)^{-1/4} = \frac{0.0395}{20.6} = 0.00192$$

$$R = (0.00192)(0.00232)(30)^2 = 0.004 \text{ psf}$$

$$\bar{V}_{\text{max}} = 37.5 \text{ fps}$$

**17:5. Pressure Drop in Pipes and Ducts.** In the design of pipe and duct systems, the primary concern of the engineer is to select a size of conduit which, taking into consideration the length of the channel and the pressure differential that is available, will deliver the fluid at the desired rate. The calculation of the pressure drop that corresponds to a given rate of flow is therefore a matter of principal importance to him.

The pressure drop must be large enough to overcome the resistance to flow offered by friction between the fluid and the walls of the passage. In addition, if there has been a significant increase in specific volume and thus in the velocity of the fluid during its flow through the pipe, the pressure drop must also account for the increased momentum of the fluid. The change of specific volume is primarily due to the lower pressure of the fluid that has resulted from the pressure drop necessary to maintain flow at the required rate. If the fluid is a liquid, or if a gas and the pressure drop is only a small fraction of the pressure at entrance to the line, the effect of increased momentum is small and may be ignored. This is the simplified form of the problem with which the engineer usually deals and will be the subject of our initial discussion.

Considering a round pipe of length  $L$ , the total force that opposes flow is the resistance multiplied by the wall area, or  $R\pi DL$ . This force is overcome by the pressure drop acting on the inside cross-sectional area of the pipe, or  $\Delta P(\pi D^2/4)$ . Therefore we may write

$$R\pi DL = \Delta P \frac{\pi D^2}{4}$$

or

$$\Delta P = \frac{4RL}{D} = \frac{4f\rho\bar{V}^2L}{D} \quad (17:6)$$

For a conduit of other than circular cross section we may write

$$R(\text{circumference})L = \Delta P(\text{cross-sectional area})$$

or

$$\Delta P = \frac{RL}{r} = \frac{f\rho\bar{V}^2L}{r} \quad (17:7)$$

in which  $r$  is the hydraulic radius, or (cross-sectional area)/(inner circumference). Equations (17:6) and (17:7) will apply to the calculation of the pressure drop in gas flow with sufficient accuracy for the usual engineering purpose if the total pressure drop does not exceed one-tenth of the absolute pressure at entrance to the line. Average values of  $f$ ,  $\rho$ , and  $\bar{V}$  are used.

The value of  $f$  in Eqs. (17:6) and (17:7) will be based on the Reynolds number. When the conduit is not circular,  $4r$  may be substituted for  $D$  in computing the Reynolds number ( $\text{Re} = 4r\bar{V}\rho/\mu$ ) if the flow is turbu-



lent, as is usually the case when the pressure drop is large enough to be important.

*Exemple 17:5.* Find the pressure drop per 100 ft length of line (a) when water at 100°F flows in a 1-in.-inside-diameter smooth tube with an average velocity of 30 fps and (b) when air initially at 14.7 psia, 70°F, flows through a smooth round duct of 1 ft diameter with an average velocity of 30 fps.

*Solution:*

(a) From Example 17:4C,  $f = 0.00164$ ;  $\rho = 1.93$ ;  $D = \frac{1}{12}$ .

$$\Delta P = \frac{4f\rho\bar{V}^2L}{D} = \frac{(4)(0.00164)(1.93)(30)^2(100)(12)}{1} = 13,600 \text{ psf} = 94 \text{ psi}$$

(b) From Example 17:4C,  $f = 0.00192$ ;  $\rho = 0.00232$ .

$$\Delta P = \frac{4f\rho\bar{V}^2L}{D} = \frac{(4)(0.00192)(0.00232)(30)^2(100)}{1} = 1.6 \text{ psf} = 0.011 \text{ psi}$$

When the fluid is a gas and the pressure drop is large, it becomes necessary to divide the entire length of pipe into shorter sections in order that the effect of change of velocity on the pressure differential that is required may be studied. In the limit, this method of dividing the passage into shorter lengths would arrive at a length  $dL$  for which the pressure change  $dP$  is to be computed. In passing through this length the velocity of the fluid increases by  $d\bar{V}$  and the momentum by  $M d\bar{V}/g$ . Applying Eq. (3:8) to a pipe of constant cross-sectional area,  $\bar{V} = Mv/A$  or, since  $M$  and  $A$  are both constant,  $d\bar{V} = (M dv/A)$ . The force acting on the cylindrical element of fluid by reason of the pressure change  $dP$  is  $A dP$ , and the frictional force  $dF$  applied at the wall surface is  $f\rho\bar{V}^2\pi D dL$ . The sum of these three forces must total zero if the pipe is horizontal, and we may write

$$A dP + \frac{M d\bar{V}}{g} + f\rho\bar{V}^2\pi D dL = 0 \quad (a)$$

Dividing each term by  $Av$  and substituting  $(M/A) dv$  for  $d\bar{V}$  and  $Mv/A$  for  $\bar{V}$ , this becomes

$$\frac{dP}{v} + \frac{1}{g} \left( \frac{M}{A} \right)^2 \frac{dv}{v} + \frac{4f(M/A)^2 dL}{gD} = 0 \quad (b)$$

Integrating between sections 1 and 2, which are a distance  $L$  apart, we have

$$\int_1^2 \frac{dP}{v} + \frac{1}{g} \left( \frac{M}{A} \right)^2 \log_e \frac{v_2}{v_1} + \frac{4f(M/A)^2 L}{gD} = 0 \quad (17:8)$$

in which  $M/A$  is the weight rate of fluid flow per unit of cross-sectional area. To evaluate the first two terms of this expression, a knowledge of

the relation between the pressure and the volume of the fluid in passage through the pipe is required. Applying Eq. (3:5) to adiabatic flow through a horizontal pipe,

$$h_1 + \frac{\bar{V}_1^2}{2Jg} = h_2 + \frac{\bar{V}_2^2}{2Jg} \quad (c)$$

or

$$h + \frac{\bar{V}^2}{2Jg} = h + \frac{1}{2Jg} \left( \frac{M}{A} \right)^2 v^2 = \text{const} = h_0 \quad (17:9)$$

in which  $h_0$  is the value approached by  $h$  as  $M/A$  approaches zero and may be readily computed based on the state of the fluid at any section of the pipe when  $M/A$  has a known value.

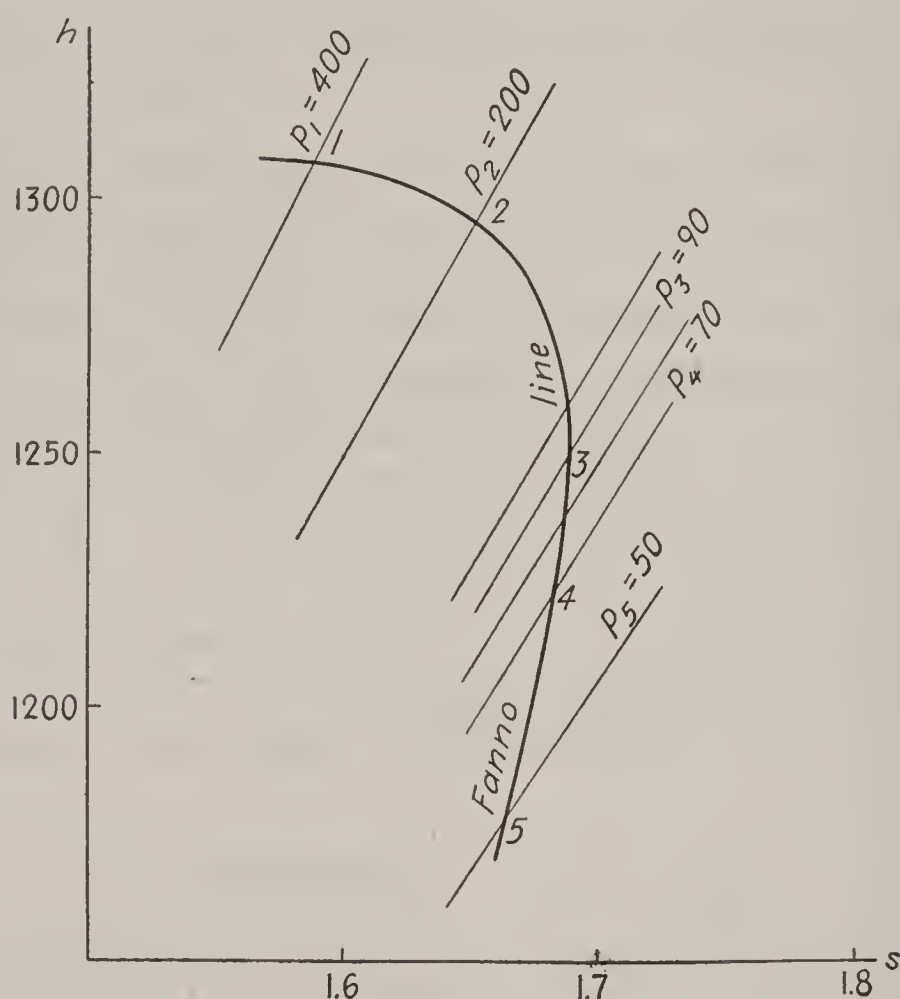


FIG. 17:4. The Fanno line.

**17:6. Fanno Lines.** When Eq. (17:9) is plotted on a Mollier chart for a given entry state 1 and flow rate  $M/A$ , as in Fig. 17:4, the resulting curve is called a Fanno line.<sup>1</sup> Points along this line indicate the state of the fluid resulting from adiabatic flow at the rate  $M/A$  as the pressure in the pipe drops from the entry pressure  $p_1$  to the successively lower pressures  $p_2$ ,  $p_3$ ,  $p_4$ , and  $p_5$ . At point 3 the path becomes vertical (isentropic) and, below that point, curves back to lower entropies. But the process is adiabatic and, according to the Second Law [see (Eq. 6:7)], the entropy

<sup>1</sup> A. Stodola, "Steam and Gas Turbines," Vol. 1, p. 61, McGraw-Hill Book Company, Inc., New York, 1927.



cannot decrease. Therefore the expansion cannot proceed beyond point 3 *within the pipe*. If a lower pressure than  $p_3$  is maintained in the space into which the pipe discharges the fluid, the pressure drop from  $p_3$  to this lower pressure must take place after the pipe exit has been passed, since it will require a larger area for fluid flow than the pipe provides. Maximum flow through the pipe is attained as the pressure in the exhaust space becomes  $p_3$ ; any further decrease of pressure in this space will not change the pressure drop in the pipe and so will not increase the rate of flow through it.

Let us suppose that maximum flow is obtained by reducing the pressure at exit from the pipe to  $p_3$ ; at point 3,  $ds = 0$ ,

$$h = u + \frac{Pv}{J} \quad dh = du + \frac{P dv}{J} + \frac{v dP}{J} = T ds + \frac{v dP}{J} = \frac{v dP}{J} \quad (\text{at point 3})$$

Differentiating Eq. (17:9),

$$dh + \frac{1}{Jg} \left( \frac{M}{A} \right)^2 v dv = \frac{v dP}{J} + \frac{1}{Jg} \left( \frac{M}{A} \right)^2 v dv = 0$$

or

$$\left( \frac{\partial v}{\partial P} \right)_s = -g \frac{1}{(M/A)^2} = -g \frac{v^2}{\bar{V}^2}$$

and

$$\bar{V}_3 = \sqrt{-gv^2 \left( \frac{\partial P}{\partial v} \right)_s}$$

From Eq. (8:25),

$$\left( \frac{\partial P}{\partial v} \right)_s = k \left( \frac{\partial P}{\partial v} \right)_T = \frac{-kP_3 v_3}{v^2}$$

and, substituting,

$$\bar{V}_3 = \sqrt{kgP_3 v_3}$$

But this is the velocity of sound in the gas at state 3, and therefore  $\bar{V}_3 = \bar{V}_s$ . When the gas enters the pipe at a velocity below the velocity of sound, the acoustic velocity is the highest velocity that can be attained within the pipe.

Points below 3 on the Fanno line of Fig. 17:4 correspond to velocities greater than the velocity of sound and cannot be reached through point 3 without allowing the gas to escape from the pipe. However, if the gas enters the pipe at a velocity greater than that of sound (as at 4 or 5), it will pass through the series of states that are connected by the Fanno line but in the reverse direction (toward increased pressure and entropy). Thus friction in the pipe will bring about a rise in pressure if the velocity exceeds the acoustic velocity. Point 3 is again the limit of this process since beyond that point the entropy decreases. If the pressure in the

space into which the pipe discharges is higher than  $p_3$ , the last stage of the compression must take place after the gas has left the pipe.

*Example 17:6A.* Plot the Fanno line for the flow of steam with  $M/A = 300$  lb/(sec)(ft<sup>2</sup>). At section 1, the pressure is 400 psia and the temperature 600°F.

*Solution:*

$p_1 = 400 \text{ psia}; t_1 = 600^\circ\text{F}; v_1 = 1.4770 \text{ ft}^3; h_1 = 1306.9 \text{ Btu}; s_1 = 1.5894$

$\bar{V}_1 = \frac{M}{A} v_1 = (300)(1.4770) = 443 \text{ fps}$

$h_0 = h_1 + \frac{1}{2Jg} \left( \frac{M}{A} \right)^2 v_1^2 = 1306.9 + \frac{(300)^2(1.4770)^2}{50,000} = 1310.8 \text{ Btu}$

Let  $p_2 = 200$  psia. The pressure has been halved, and, for a trial, we shall assume that the specific volume, and therefore the velocity, has been doubled. Then the trial value of  $h_2$  is  $h_0 - \frac{\bar{V}_2^2}{2Jg} = 1310.8 - \frac{(300)^2(2 \times 1.4770)^2}{50,000} = 1295.1 \text{ Btu}$ . At 200 psia, this enthalpy lies between temperatures of 540 and 560°F. Making trial calculations at each of these temperatures, for 540°F

$h_0 = 1290.5 + \frac{(300)^2(2.862)^2}{50,000} = 1305.3 \text{ Btu}$

and for 560°F

$h_0 = 1301.1 + \frac{(300)^2(2.928)^2}{50,000} = 1316.5 \text{ Btu}$

Interpolating for the required value of  $h_0 = 1310.8$ , the temperature  $t_2$  is found to be about 550°F, and the other properties are  $v_2 = 2.895$ ;  $h_2 = 1295.8$ ;  $s_2 = 1.6513$ . Checking,

$h_0 = 1295.8 + (1.8)(2.895)^2 = 1310.8$

This locates a second point on the Fanno line. The velocity  $\bar{V}_2 = (M/A)v_2 = (300)(2.895) = 870 \text{ fps}$ . Proceeding in like manner, the following table may be prepared from which the Fanno line may be plotted, as in Fig. 17:4. The pressures of 100 and 80 psia have been added to the table to show more clearly the point at which the Fanno line becomes vertical. Checking at point 3 (90 psia) for  $\bar{V}_s$ .

$\bar{V}_s = \sqrt{kgP_3v_3} = \sqrt{(1.3)(32.2)(90)(144)(5.806)} = 1775 \text{ fps}$

This is close to the velocity  $\bar{V}_3$  but indicates that the point at which the Fanno line becomes vertical lies at a pressure slightly below 90 psia.

DATA FOR FANNO LINE  
 $M/A = 300; p_1 = 400 \text{ psia}; t_1 = 600^\circ\text{F}$

Station	Pressure, psia	Tempera- ture, °F	Enthalpy, Btu	Volume, ft <sup>3</sup> /lb	Entropy	Velocity, fps
1	400	600	1306.9	1.4770	1.5894	443
2	200	550	1295.8	2.895	1.6513	870
	100	461	1259.3	5.339	1.6874	1600
3	90	441	1250.3	5.806	1.6889	1745 = $\bar{V}_s$ approx
	80	415	1238.3	6.342	1.6879	1905
4	70	382.5	1223.2	6.974	1.6848	2090
5	50	287.5	1177.6	8.603	1.6632	2580



The relation between the pressure and the volume that must be known if Eq. (17:8) is to be of use is based on the Fanno-line relation [Eq. (17:9)]. It has been shown (Example 2:9) that it is possible to express the enthalpy of a perfect gas in the form

$$h = A + EPv \quad (17:10)$$

in which  $A$  and  $E$  are constants.<sup>1</sup> This relation may also be applied with fair accuracy to a wider range of gases and vapors, provided that the values of the constants are established from data at states close to those in the range over which the equation is to be applied. Making this substitution in Eq. (17:9), we have

$$A + EPv + \frac{1}{2Jg} \left( \frac{M}{A} \right)^2 v^2 = h_0 \quad (17:11)$$

This is a quadratic equation of the form

$$av^2 + EPv + c = 0 \quad (17:12)$$

where  $a = \frac{1}{2Jg} \left( \frac{M}{A} \right)^2$  and  $c = A - h_0$ . All quantities in Eq. (17:12) are constants except  $v$  and  $P$ . Solving for  $P$  in terms of  $v$ ,

$$P = -\frac{a}{E}v - \frac{c}{E}\frac{1}{v}$$

$$dP = -\frac{a}{E}dv + \frac{c}{E}\frac{dv}{v^2}$$

Substituting this value in the first term of Eq. (17:8) and integrating,

$$\int_{v_1}^{v_2} \frac{dP}{v} = -\frac{a}{E} \int_{v_1}^{v_2} \frac{dv}{v} + \frac{c}{E} \int_{v_1}^{v_2} \frac{dv}{v^3} = -\frac{a}{E} \log_e \frac{v_2}{v_1} - \frac{\frac{1}{2}c}{E} \left( \frac{1}{v_2^2} - \frac{1}{v_1^2} \right) \quad (17:13)$$

When this value is substituted for the first term of Eq. (17:8), that equation may be used for the computation of the coefficient of friction in the flow of compressible fluids; measurements of the mass rate of flow and data with respect to the state at entrance and the pressure at exit from a section of the pipe of measured length will be sufficient to enter the equation. In obtaining the values of  $v_1$  and  $v_2$  for substitution, we may return to the quadratic [Eq. (17:12)] and, solving it, obtain

$$v = \frac{-EP \pm \sqrt{E^2P^2 - 4ac}}{2a} \quad (17:14)$$

*Example 17:6B.* Steam is supplied to a length of 1-in. commercial pipe from a tank. The pressure in the tank is steadily maintained at 40 psia, the temperature is 300°F,

<sup>1</sup>  $A$  as in Eq. (1:7);  $E = \frac{B}{144} + \frac{1}{J}$  with  $B$  as in Eq. (1:7).

and the steam velocity is negligible. The pressure at an upstream pipe section 1 is 35 psia and, at a second section located 36 ft downstream from section 1, is 25 psia. The weight of steam flow through the pipe is 10 lb/min. The pipe is well insulated, and the flow may be considered to be adiabatic. Calculate the value of the friction coefficient, and compare with that obtained from Eq. (17:5).

*Solution.* Commercial 1-in. pipe has an internal diameter of 1.05 in. and an internal transverse area of 0.006 ft<sup>2</sup>.

$$\frac{M}{A} = \frac{10}{(60)(0.006)} = 27.75 \text{ lb}/(\text{sec})(\text{ft}^2); h_0 = h \text{ at } 40 \text{ psia, } 300^\circ\text{F} = 1186.8 \text{ Btu}$$

Using the method outlined in Example 17:6A, the following data may be calculated:

$$p_1 = 35; t_1 = 292.7^\circ\text{F}; h_1 = 1184.4; v_1 = 12.525; s_1 = 1.7105; \bar{V}_1 = 347 \text{ fps}$$

$$p_2 = 25; t_2 = 283.1^\circ\text{F}; h_2 = 1182.2; v_2 = 17.410; s_2 = 1.7439; \bar{V}_2 = 483 \text{ fps}$$

Using these data to determine  $A$  and  $E$  in Eq. (17:10),

$$1184.4 = A + E(35)(144)(12.525)$$

$$1182.2 = A + E(25)(144)(17.410)$$

from which

$$E = 0.004 \text{ and } A = 931.7$$

$$a = \frac{27.75^2}{50,000} = 0.0154; c = 931.7 - 1186.8 = -255.1$$

Substituting in Eq. (17:8),

$$-\frac{0.0154}{0.004} \log_e \frac{17.410}{12.525} - \frac{1}{2} \left( \frac{-255.1}{0.004} \right) \left( \frac{1}{17.410^2} - \frac{1}{12.525^2} \right) + \left( \frac{1}{32.2} \right) (27.75)^2 \log_e \frac{17.410}{12.525} + \frac{4f(27.75)^2(12)(36)}{(32.2)(1.05)} = 0$$

or

$$-1.27 - 96.5 + 7.9 + 39,400f = 0 \text{ and } f = 0.00228$$

$$\mu = 3 \times 10^{-7} \text{ lb-sec}/\text{ft}^2$$

[Table 6, steam tables]

$$\rho = \frac{1}{vg} = \frac{1}{(15)(32.2)} = 0.00207$$

$$\text{Re} = \frac{\bar{V}D\rho}{\mu} = \frac{(415)(1.05)(0.00207) \times 10^7}{(12)(3)} = 250,000$$

$$f = (0.0395)(250,000)^{-\frac{1}{4}} = 0.00177$$

[Eq. (17:5)]

It will be noted that this calculation has been based on the use of average values of the specific volume, the viscosity, and the velocity. The value of  $f$  that is obtained from the assigned data is about 30 per cent higher than the value obtained from Eq. (17:5), which applies to smooth tubes. This is a reasonable allowance for the roughness factor of 1-in. commercial pipe.

**17:7. The Rayleigh Line.** Pressure shock (see Art. 11:7) is the name given a sudden rise in pressure which is sometimes observed in the diverging section of a nozzle. Observation indicates that the fluid always enters this compression wave at a velocity greater, and leaves it at a velocity less, than that of sound and that, for steadily maintained supply conditions and exhaust pressure, the wave remains stationary in the channel.



The pressure rise takes place so sharply that the divergence of the channel may be ignored and the flow may be compared with that in a very short length of pipe. Because the channel section is so short, wall friction may also be neglected and Eq. (a) of Art. 17:5 may be written as

$$A \, dP + \frac{M}{g} \, d\bar{V} = 0$$

Designating the entry section as  $a$  and the exit section from the shock wave as  $b$ , integration gives

$$A(P_b - P_a) + \frac{M}{g} (\bar{V}_b - \bar{V}_a) = 0$$

or, since  $\bar{V} = (M/A)v$ ,

$$P_b = P_a - \frac{1}{g} \left(\frac{M}{A}\right)^2 (v_b - v_a) \tag{17:15}$$

Beginning with the known values of  $P$  and  $v$  at  $a$  and assuming successively lower values of  $v_b$ , this relation may be plotted on a Mollier chart, as in

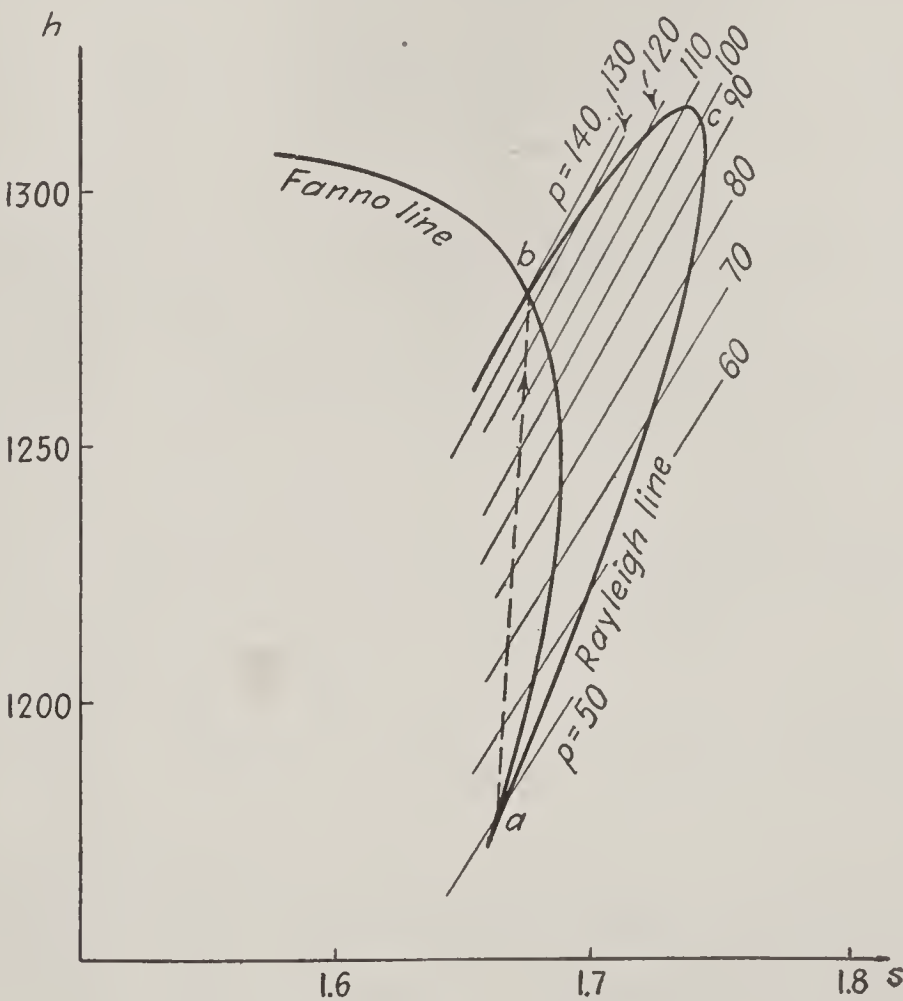


FIG. 17:5. The Rayleigh line.

Fig. 17:5; it is represented by the curve  $acb$  of that figure and is called a *Rayleigh line*. Also shown in Fig. 17:5 is a Fanno line which has been drawn through state  $a$  for the same flow rate  $M/A$  as applies along the Rayleigh line. The two curves again intersect at state  $b$ .

The fluid cannot progress through the series of states that are connected by the Rayleigh line without heat flow; yet the flow through the channel is adiabatic. However, at state  $b$  the Rayleigh line returns to intersect again the Fanno line, which connects states assumed in adiabatic flow. State  $b$  is consequently not inconsistent with the requirement that the flow be adiabatic; it is therefore a possible state to which the fluid may suddenly shift. The pressure at  $b$  will always be higher than at point  $a$ ; the same is true of the entropy. The sudden change from state  $a$  to state  $b$  is possible only because the entropy has increased during this adiabatic process; a change in the opposite direction (from  $b$  to  $a$ ) would, according to the Second Law, be inconceivable, and this explains why the pressure is always observed to rise, never to fall, in these shock waves.

To find the second point of intersection of the Rayleigh and Fanno lines at state  $b$ , we may assume as before that Eq. (17:10) provides a sufficiently accurate relation and write

$$h_b = A + EP_b v_b \quad (17:16)$$

Substituting this value of  $h_b$  in the equation of the Fanno line [Eq. (17:9)] we have

$$A + EP_b v_b + \frac{1}{2Jg} \left( \frac{M}{A} \right)^2 v_b^2 = h_0$$

or

$$P_b = \frac{h_0 - A}{Ev_b} - \frac{1}{2JgE} \left( \frac{M}{A} \right)^2 v_b = -\frac{c}{E} \frac{1}{v_b} - \frac{a}{E} v_b \quad (17:17)$$

Equating this value of  $P_b$  to that of Eq. (17:15),

$$-\frac{c}{E} \frac{1}{v_b} - \frac{a}{E} v_b = P_a - 2Jav_b + 2Jav_a \quad (17:18)$$

Multiplying by  $Ev_b$ , rearranging, and changing signs,

$$(a - 2JaE)v_b^2 + (EP_a + 2JaEv_a)v_b + c = 0 \quad (17:19)$$

This is the quadratic form and can be solved for  $v_b$ . Values of  $P_b$  and  $h_b$  may be computed by substitution in Eqs. (17:17) and (17:16) in that order.

*Example 17:7.* Plot a Rayleigh line for  $M/A = 300$  lb/(sec)(ft<sup>2</sup>) which passes through state 5 of the Fanno line of Example 17:6A. Find the second intersection with the Fanno line of that example.

*Solution:*

$$P_a = P_5 = (50)(144) = 7200 \text{ psf}; v_a = v_5 = 8.603 \text{ ft}^3/\text{lb}$$

A series of points on the Rayleigh line will be based on arbitrarily assumed increasing pressures until the second point of intersection with the Fanno line is reached. To check the location of that point, Eq. (17:19) will be solved for  $v_b$ . Increasing pressures are assumed instead of decreasing volumes since they offer a more convenient



key with which to enter the steam tables for interpolation. A sample calculation is shown below.

Assume  $p_b = 70$  psia. Substituting in Eq. (17:15),

$$(70)(144) = (50)(144) - \frac{300^2}{32.2} (v_b - 8.603) \text{ or } v_b = 7.573 \text{ ft}^3/\text{lb}$$

Taking a pressure of 70 psia and specific volume of 7.573 ft<sup>3</sup>/lb to Table 3 of the steam tables, interpolation gives the temperature as 448°F, the enthalpy as 1256.2 Btu, and the entropy as 1.7224. Following this method for successively higher pressures, the following table is prepared:

DATA FOR RAYLEIGH LINE  
 $M/A = 300; p_a = 50; v_a = 8.603$

Station	Pressure, psia	Volume, ft <sup>3</sup> /lb	Temp., °F	Enthalpy, Btu	Entropy
<i>a</i>	50	8.603	287.5	1177.6	1.6632
	60	8.088	375	1221.0	1.6986
	70	7.573	448	1256.2	1.7224
	80	7.058	505	1283.5	1.7371
	90	6.548	546	1303.9	1.7443
	100	6.033	570	1314.4	1.7439
	110	5.518	578	1317.4	1.7366
	120	5.003	569	1312.2	1.7221
	130	4.483	543	1298.2	1.6997
	140	3.973	504	1277.3	1.6705
<i>b</i>	139	4.04	512	1281.4	1.6756

The data of the second to the ninth lines of the table have been obtained by the method of calculation outlined above. The data have been used to plot points on the Mollier chart of Fig. 17:5, and these points have been connected to form the required Rayleigh line. It was found that this line recrossed the Fanno line between pressures of 130 and 140 psia. To check the point of intersection, resort was made to Eq. (17:19). To obtain  $A$  and  $E$  for use in that equation, the two states selected were state  $a$  and the state, lying near the second intersection, where  $p = 140$  psia,  $v = 3.973$  (see table above). Then, applying Eq. (17:10),

$$\begin{aligned} 1177.6 &= A + E(50)(144)(8.603) \\ 1277.3 &= A + E(140)(144)(3.973) \end{aligned}$$

and, solving,

$$E = 0.0055; A = 837.0$$

Also,

$$a = \frac{300^2}{50,000} = 1.8; c = 837.0 - 1310.8 = -473.8$$

$$\begin{aligned} a + 2JaE &= 1.8 - (2)(778)(1.8)(0.0055) = -13.62 \\ EP_a + 2JaEv_a &= (0.0055)(50)(144) + (2)(778)(1.8)(0.0055)(8.603) = 172.1 \end{aligned}$$

Changing signs, Eq. (17:19) becomes

$$13.62v_b^2 - 172.1v_b + 473.8 = 0$$

or, solving for  $v_b$ ,

$$v_b = \frac{172.1 \pm \sqrt{172.1^2 - (4)(13.62)(473.8)}}{(2)(13.62)} = 4.04$$

This volume has been used in calculating the data for the last line of the table, giving the properties at the second point of intersection. The pressure at entrance to the wave defined by this Fanno-Rayleigh line combination is 50 psia, and the velocity (see table of Example 17:6A) is 2580 fps, well above the velocity of sound. At exit from the wave, the pressure has risen sharply to 139 psia, and the velocity is

$$\bar{V}_b = \frac{M}{A} v_b = (300)(4.04) = 1212 \text{ fps}$$

This velocity is well below the velocity of sound. It will also be noted that  $s_b > s_a$ .

### Problems

1. Show that the unit of viscosity used in Table 6 of the Keenan and Keyes steam tables (lb-sec/ft<sup>2</sup>) is equal to 47,800 centipoises.

2. A thin rectangular plate 50 by 70 in. is immersed in a stream of lubricating oil (SAE 30). What is the viscous drag on the plate in pounds if the velocity gradient at the surface of the plate is 5 fps/in.? Assume  $t = 70^\circ\text{F}$ .

3. The viscous drag forms a part of the total drag of an airplane wing and is often called the "skin-friction" drag. It is calculated from the following equation:

$$D_f = C_f \frac{\rho}{2} S \bar{V}^2$$

in which  $D_f$  = skin-friction drag, lb

$C_f$  = dimensionless coefficient

$\rho$  = mass density of air, slugs/ft<sup>3</sup>

$S$  = projected area of wing (area of one side, approximately), ft<sup>2</sup>

$\bar{V}$  = air speed relative to wing, fps

If  $C_f = 0.006$ , and the wing is rectangular, 30 ft from tip to tip and 5 ft from leading to trailing edge, what is the skin-friction drag of the wing in flying through air at standard atmospheric pressure and a temperature of  $59^\circ\text{F}$  at a speed of 100 mph? Based on Eq. (17:1), find the velocity gradient at the surface of the wing.

4. Employ dimensional analysis to show that the dimensionless coefficient  $C_f$  in the formula presented in Prob. 3 for the calculation of drag due to skin friction is a function of the Froude number ( $\bar{V}^2/Lg$ ). Assume that the factors affecting the drag are a dimension of the wing ( $L$ ), the velocity of the air stream ( $\bar{V}$ ), the mass density of the air ( $\rho$ ), and the acceleration due to gravity ( $g$ ).

5. Show that if the velocity of sound is added to the list of factors affecting the resistance to flow [see Eq. (1), Art. 17:3], the coefficient of friction becomes a function of the Mach number as well as the Reynolds number.

6. Prove that the kinetic energy for laminar flow in a pipe, assuming a parabolic velocity profile, is  $\bar{V}_{av}^2/g$  per pound.

7. What average velocity is equivalent to  $\text{Re} = 2000$  in the flow of SAE 30 lubricating oil at a temperature of  $100^\circ\text{F}$  (density = 57 lb/ft<sup>3</sup>) in a 1-in. pipe? What is the maximum velocity? Repeat for a  $\frac{1}{2}$ -in. pipe (internal diameter = 0.62 in.).

8. Check Fig. 17:3 at Reynolds numbers of 1000, 2000, 4000, and 10,000. Calculate the friction coefficient for a smooth tube at a Reynolds number of 100,000.

9. Compare the values of the friction coefficients for smooth tubes as obtained



from the Blasius and the Nikuradse equations at a Reynolds number of 4000. At  $Re = 10,000$ . At  $Re = 100,000$ .

10. Calculate the total drag in a 100-ft length of commercial 1-in. pipe when it carries water at  $60^{\circ}\text{F}$  and  $Re = 2000$ . What weight of water is handled per hour? Repeat for  $Re = 10,000$ . Note that this is commercial pipe. What differential of pressure must be maintained between the ends of the pipe in each case?

11. Air at  $130^{\circ}\text{F}$ , 14.7 psia, moves through a smooth duct of 2 ft inside diameter at a Reynolds number of 200,000. The duct is 100 ft in length. Assume that the temperature of the air does not change in passage through the duct. (a) Calculate the total drag, assuming that the velocity is the same at all sections. (b) What volume, in cubic feet per minute, is handled? (c) What is the pressure drop? (d) What power is required? (e) What percentage change in velocity would actually be realized if account is taken of the compressibility of the air?

12. (a) Repeat Prob. 11 for a duct 2 ft square in section. (b) For a rectangular duct 10 by 20 in.

13. Air at  $100^{\circ}\text{F}$ , 15 psia, enters a 12- by 20-in. rectangular smooth duct 100 ft long. At exit, the pressure is 14.9 psia, and the temperature is  $96^{\circ}\text{F}$ . What weight of air is handled per minute? (Note: Assume a reasonable value for  $Re$ , and check the calculated velocity against your assumption, making a new estimate if necessary.)

14. The water pressure in a street service main is 60 psia. It is desired to choose a size for a branch line such that it will be capable of delivering at least  $4\text{ ft}^3$  of water per minute to a residence. The branch will have an equivalent length of 100 ft. (The equivalent length of line allows for the resistance of fittings, etc., by expressing this resistance in terms of lengths of straight pipe.) Add 30 per cent to  $f$  to allow for roughness of commercial pipe. What size of commercial steel pipe is required? Refer to a handbook for the dimensions of commercial pipe.

15. Show that the dimensions of each term of Eq. (17:8) are the same.

16. Solve Example 17:6A when (a)  $M/A = 1500\text{ lb}/(\text{sec})(\text{ft}^2)$  and (b) when  $M/A = 1280\text{ lb}/(\text{sec})(\text{ft}^2)$ . Plot these Fanno lines and the Fanno line of Example 17:6A on the same graph.

17. As  $M/A$  approaches 0, what locus is approached by the Fanno line?

18. Steam enters a pipe with an internal diameter of 2 in. from a large tank in which its pressure is 100 psia, its temperature is  $400^{\circ}\text{F}$ . At a certain section of the pipe, the pressure has decreased to 80 psia, the temperature to  $390^{\circ}\text{F}$ . Assuming the flow to be adiabatic, what weight of steam per minute is carried by the pipe? If this flow through the pipe is a maximum, what are the pressure and temperature of the steam at its exit?

19. Steam is withdrawn from a large tank in which its pressure is 100 psia and its temperature  $400^{\circ}\text{F}$  through a well-insulated pipe with an internal diameter of 2 in. The rate of steam flow is 75 lb/min. At a certain section of the pipe, the pressure is 80 psia. What is the temperature at this section? At a section that is 85 ft farther downstream, the pressure is found to be 60 psia. What is the temperature at this second section? What is the coefficient of friction?

20. Air is withdrawn from a large tank, in which its pressure is 100 psia and its temperature  $400^{\circ}\text{F}$ , through a well-insulated pipe with an internal diameter of 2 in. The rate of air flow is 75 lb/min. At a certain section of the pipe, the pressure is 80 psia. What is the temperature at this section? At a section farther downstream, the pressure of the air is 60 psia. If the average value of  $f$  between the two sections is 0.0018, what is the distance between them?

21. Plot a Rayleigh line for  $M/A = 300\text{ lb}/(\text{sec})(\text{ft}^2)$  which passes through state 4 of the Fanno line of Example 17:6A. Find the second intersection with the Fanno line.

## Symbols

$a, b, c, d, e$	constants
$A$	area; also, a constant
$B$	a constant
$C$	a dimensionless constant
$D$	a dimension of the channel; for round pipes, the diameter
$E$	a constant
$f$	a function
$f$	coefficient of friction
$F$	force; also, the dimension of force
$g$	acceleration of gravity
$h$	specific enthalpy
$J$	proportionality factor
$L$	length; also, the dimension of length
$M$	mass rate of flow; also, the dimension of mass
$p$	pressure, psi
$P$	pressure, psf; pressure in general
$r$	hydraulic radius
$R$	force per unit area of wetted surface; also, the gas constant
Re	Reynolds number
$s$	specific entropy
$T$	absolute temperature
$v$	specific volume
$V$	volume
$V$	velocity
$\bar{V}_s$	velocity of sound
$y$	thickness of a fluid lamination

*Greek Letters*

$\theta$	the dimension of time
$\mu$	coefficient of viscosity
$\rho$	mass density



## CHAPTER 18

### REAL GASES

**18:1. Introduction.** The fluids with which we have been concerned in preceding chapters may be put into two classifications. They either were perfect gases or were fluids, which, like steam, are important enough to the engineer and vary sufficiently from the behavior of a perfect gas in the range of states of engineering interest to warrant the extensive research that is required to prepare special equations of state and, from these equations, tables of properties. Our purpose in restricting ourselves to these two classes of fluids has been to avoid complications and distractions in the development of basic thermodynamic theory. In line with that purpose, we have further simplified the handling of a perfect gas by assuming that its specific heats are constant although, as shown in Chap. 9, there is no reason why the specific heat of even a perfect gas may not be a function of the temperature. For this reason, equations such as (9:27) to (9:43) must be regarded as only approximations as they apply to the real gas, even when the fluid is one of the “permanent” gases. Whether these equations, as written, are sufficiently accurate for the engineer’s purposes will depend upon the degree of accuracy that is required. In addition, it may be necessary to deal with fluids which, in the range of states of interest, are close to the two-phase region where the perfect-gas relation is entirely inadequate; if special tables of properties are not available to his use, nothing in preceding chapters would equip the engineer to deal with a situation of this kind. Although a full treatment of the subject is beyond the scope of this text, it will be the purpose of the present chapter to introduce the reader to the methods which are applied in such circumstances.

**18:2. The Perfect Gas with Variable Specific Heat.** At low pressure the perfect-gas relation will, for all gases, hold to a high degree of accuracy. Even when the pressure is a considerable fraction of the critical pressure but the temperature is high as compared with the critical temperature, its accuracy is often satisfactory for the purposes of the engineer and he may treat the gas as a perfect gas.

That he considers the perfect-gas relation,  $Pv = RT$ , a sufficiently accurate relation to apply to the situation at hand does not, however, mean that the engineer may safely take the further step of assuming constant specific heats in simplifying his problem. Note, however, that if the perfect-gas relation is assumed to hold, the variation of specific heat

TABLE 18:1. EQUATIONS FOR SPECIFIC HEAT AT CONSTANT PRESSURE

Eq. No.	Gas	Mol. wt	Molar specific heat at constant pressure, $mc_p$ , Btu/(mole)(°R) ( $T$ in °R)	Range, °R	Max error, %
(1)* (2)† (3)‡ (4)‡	O <sub>2</sub>	32.00	6.40 + 0.00113 $T$ 6.93 + 0.0000001254 $T^2$ 11.515 - 172 $T^{-\frac{1}{2}}$ + 1530 $T^{-1}$ 11.515 - 172 $T^{-\frac{1}{2}}$ + 1530 $T^{-1}$ + (0.00005)( $T$ - 5000)	720-1900 Not stated 540-5000 5000-9000	1 Not stated 1.1 0.3
(5)* (6)† (7)‡	N <sub>2</sub>	28.02	6.26 + 0.000818 $T$ 6.93 + 0.0000001254 $T^2$ 9.47 - 3470 $T^{-1}$ + 1,160,000 $T^{-2}$	720-1900 Not stated 540-9000	1 Not stated 1.7
(8)* (9)†	Air	28.96	6.37 + 0.000886 $T$ 6.93 + 0.0000001254 $T^2$	720-1900 Not stated	1 Not stated
(10)* (11)† (12)‡ (13)‡	H <sub>2</sub>	2.016	6.75 + 0.000230 $T$ 6.93 + 0.0000001254 $T^2$ 5.76 + 0.000578 $T$ + 20 $T^{-\frac{1}{2}}$ 5.76 + 0.000578 $T$ + 20 $T^{-\frac{1}{2}}$ - (0.00033)( $T$ - 4000)	720-1900 Not stated 540-4000 4000-9000	1 Not stated 0.8 1.4
(14)* (15)† (16)† (17)‡	CO <sub>2</sub>	44.00	8.18 + 0.00275 $T$ 7.15 + 0.0039 $T$ - 0.0000006 $T^2$ 12.196 + 0.00042 $T$ 16.2 - 6530 $T^{-1}$ + 1,410,000 $T^{-2}$	720-1900 Below 2900 Above 2900 540-6300	3 Not stated Not stated 0.8
(18)* (19)† (20)‡	CO	28.00	6.33 + 0.000898 $T$ 6.93 + 0.0000001254 $T^2$ 9.46 - 3290 $T^{-1}$ + 1,070,000 $T^{-2}$	720-1900 Not stated 540-9000	1 Not stated 1.1
(21)* (22)† (23)‡	H <sub>2</sub> O	18.016	7.80 + 0.000299 $T$ 7.80 + 0.0003 $T$ + 0.000000315 $T^2$ 19.86 - 597 $T^{-\frac{1}{2}}$ + 7500 $T^{-1}$	720-1900 Not stated 540-5400	Not stated Not stated 1.8
(24)* (25)† (26)‡ (27)‡ (28)‡ (29)‡ (30)*	CH <sub>4</sub>   C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>6</sub> C <sub>8</sub> H <sub>16</sub> C <sub>8</sub> H <sub>18</sub>	16.03   28.03 30.05 112.3 114.1	3.33 + 0.00899 $T$ 3.459 + 0.01056 $T$ 4.52 + 0.00737 $T$ 4.23 + 0.01177 $T$ 4.01 + 0.01636 $T$ 7.92 + 0.0601 $T$ 11.98 + 0.00555 $T$	720-1900 Not stated 540-1500 350-1100 400-1100 400-1100 720-1900	Not stated Not stated 1.2 1.5 1.5 4 Not stated

\* Adapted from *NACA Rept.* 699 (1940).  
† Marks, "Mechanical Engineers' Handbook," 5th ed., McGraw-Hill Book Company, Inc., New York, 1951.  
‡ Sweigert and Beardsley, "Empirical Specific Heat Equations Based on Spectroscopic Data" (at zero pressure), *Georgia School Technol. State Eng. Expt. Sta. Bull.* 1, No. 3 (1938).



is only with temperature and is independent of the pressure. Moreover, the difference, at any given state, between the specific heat at constant pressure and the specific heat at constant volume must always equal  $R$ , itself a constant.

Equations for the specific heats of real gases are based on experimental data obtained by various methods of approach. Being experimentally derived, they must be regarded as only closer approximations than the use of a constant value for the specific heat. The specific heat of the multiatomic gas that follows the perfect-gas relation has been shown in Chap. 9 to increase with temperature. Empirical equations that express its value must reflect this requirement if they are to be considered consistent. These equations are in various forms; three typical forms are listed below,

$$c_p = A + BT + CT^2 \quad (1)$$

$$c_p = A + BT^{-\frac{1}{2}} + CT^{-1} + D(T - E) \quad (2)$$

$$c_p = A + BT^{-1} + CT^{-2} \quad (3)$$

in which  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  are constants. Of these constants,  $B$ ,  $C$ ,  $D$ , and  $E$  may have zero values in a specific equation or may be negative. For example, it will be noted that if the specific heat is to show the characteristic increase with temperature, either  $B$  or  $C$ , or both, must be negative in (3). An equation of the form of (1), but with  $C = 0$ , is usually satisfactory to yield the degree of accuracy required in engineering calculations. Table 18:1 lists a number of equations from various sources from which a choice may be made according to the degree of accuracy desired. The equations based on spectroscopic data cover a wider temperature range and are credited with being the most precise; they are also, in general, the most complicated from the standpoint of ease of use in establishing thermodynamic relations between primary and secondary properties. All of the tabulated equations give the molar specific heat at constant pressure [Btu/(mole)(°R)]; to obtain the specific heat per pound, each constant must be divided by the molecular weight of the gas. The equation for the specific heat at constant volume may be established from these expressions by deducting the quotient obtained by dividing the universal gas constant by  $J$ , or  $mR/J = \frac{1.545}{778} = 1.985$ , from the constant term ( $A$ ). Thus, from Eq. (1) of Table 18:1, the equation for the molar specific heat at constant volume of  $O_2$  may be written as

$$mc_v[\text{Btu}/(\text{mole})(^\circ\text{R})] = (6.40 - 1.985) + 0.00113T = 4.415 + 0.00113T$$

The introduction of a variable specific heat which is a function of the temperature alone brings about certain changes in the equations for the heat flow and work that accompany a perfect-gas reversible process and the expressions which define the change of internal energy, enthalpy, and entropy.

*Changes of Enthalpy and Internal Energy.* It has been shown [Eq. (9:13)] that  $dh = c_p dT$  for the perfect gas. When  $c_p$  is constant,  $h_2 - h_1 = c_p(T_2 - T_1)$ . Remembering that  $c_p$  is now, though variable, a function of  $T$  alone, we may write

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT \quad (18:1)$$

The indicated integration cannot, of course, be performed until an expression which defines  $c_p$  in terms of  $T$  is available. Similarly, based on Eq. (9:12),

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT \quad (18:2)$$

*Changes of Entropy.* The changes of enthalpy and of internal energy are functions of the temperature alone, but the change of entropy is a function of pressure as well as temperature. It has been shown in Art. 8:1 that  $T ds = dh - v dP/J$ . For the perfect gas this may be changed to the form

$$T ds = c_p dT - \frac{v dP}{J}$$

or

$$ds = \frac{c_p dT}{T} - \frac{v dP}{JT} = \frac{c_p dT}{T} - \frac{R dP}{J P} \quad (18:3)$$

Integrating,

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - \frac{R}{J} \int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{c_p dT}{T} - \frac{R}{J} \log_e \frac{P_2}{P_1} \quad (18:4)$$

*Work and Heat Flow for the Reversible Process.* For our purpose, reversible processes will be classified as constant-pressure, constant-volume, isothermal, adiabatic, and polytropic, as in Chap. 9 and Table 9:1. Each is discussed separately below:

1. Constant-pressure ( $n = 0$ ). The final pressure, temperature, and volume may be found from the perfect-gas relation, and the expressions in the third, fourth, and fifth columns of Table 9:2 may be used. The heat supplied the system is equal to the change of enthalpy, or

$${}_1Q_2 = M \int_{T_1}^{T_2} c_p dT$$

The work is, as in Table 9:2,  ${}_1W_2 = P(V_2 - V_1)$ .

2. Constant volume ( $n = \infty$ ). Table 9:2 may be used to find the final pressure, temperature, and volume. The heat flow is equal to the change of internal energy, or

$${}_1Q_2 = M \int_{T_1}^{T_2} c_v dT$$

The work is zero.



3. Isothermal ( $n = 1$ ). Table 9:2 may be used to find the final pressure, temperature, and volume. There is no change in internal energy since the internal energy is still a function of temperature alone. The heat flow and the work may also be based directly on the information presented in Table 9:2.

4. Reversible adiabatic. This process follows a path defined as  $PV^k = \text{const}$  as before, but there is an important difference, for  $k$  is no longer a constant. This follows from the change which is now taking place in both  $c_p$  and  $c_v$  with temperature, while the difference between them remains constant. Table 9:2 therefore cannot be used to locate the final pressure, temperature, or volume, nor can the expression for work presented in that table be applied. The heat flow is zero by definition of the adiabatic, and this means, for the reversible process, that the entropy is constant. We may therefore write Eq. (18:3) in the form

$$ds = \frac{c_p dT}{T} - \frac{R}{J} \frac{dP}{P} = 0$$

and, integrating,

$$\log_e \frac{P_2}{P_1} = \frac{J}{R} \int_{T_1}^{T_2} \frac{c_p dT}{T} \quad (18:5)$$

This equation provides the means of establishing a relation between the change of pressure and the change of temperature. The perfect-gas relation may now be used to fix the final volume. The work is equal to the decrease of internal energy and may be calculated by applying Eq. (18:2).

5. Polytropic ( $n = \text{const}$ ). As indicated in the heading, the polytropic for the perfect gas with variable specific heats is defined as a reversible process following a path represented by the equation  $PV^n = \text{const}$ , with  $n$  a constant. No longer does this also mean that the amount of heat flow accompanying a unit change in temperature is the same throughout the process, as is the case when  $c_p$  and  $c_v$  are constant (see Art. 9:5). However, since the path is established, Table 9:2 may be used to find the final pressure, temperature, and volume, as for (1), (2), and (3) above. Also, again because the path is known, the use of that table for the calculation of the amount of work is made possible. When Eq. (18:2) has been used to compute the change of internal energy, the heat flow is obtained from the simple addition of the work and the change of internal energy, as based on Eq. (2:3).

The observant reader will have noted that the use of specific heats which are functions of the temperature has added little to the difficulty of solution of the reversible process for a perfect gas except in the evaluation of  $\int_{T_1}^{T_2} c_p dT$ ,  $\int_{T_1}^{T_2} c_v dT$ , and  $\int_{T_1}^{T_2} \frac{c_p dT}{T}$ . The amount of time and labor

required in the evaluation of these quantities depends upon the form of the expression for  $c_p$  ( $c_v$ , it will be remembered, differs only in the constant term) and explains why an expression of the form  $c_p = A + BT$  is favored for many engineering calculations where extreme accuracy is not necessary.

*Example 18:2.* A pound of air is adiabatically and reversibly compressed from an initial state at which  $p_1 = 14.7$  psia,  $t_1 = 40^\circ\text{F}$ , to a final pressure  $p_2$  of 75 psia. (a) Assuming the specific heat to be expressed by Eq. (8) of Table 18:1, calculate the final temperature, the change of enthalpy, internal energy, and entropy, and the work done on the air. (b) Compare with the same quantities as calculated by assuming constant specific heats as in Table 9:1.

*Solution:*

(a) From Eq. (18:5),

$$\begin{aligned}\log_e \frac{75}{14.7} &= 1.63 = \frac{778}{53.3} \int_{500}^{T_2} \frac{(6.37 + 0.000886T) dT}{28.96T} \\ &= (0.504) \left[ 6.37 \log_e \frac{T_2}{500} + 0.000886(T_2 - 500) \right]\end{aligned}$$

Solving,

$$T_2 = 797^\circ\text{R}$$

From Eq. (18:1),

$$\begin{aligned}h_2 - h_1 &= \frac{1}{28.96} \int_{500}^{797} (6.37 + 0.000886T) dT = \left( \frac{1}{28.96} \right) [6.37T + 0.000443T^2]_{500}^{797} \\ &= \left( \frac{1}{28.96} \right) [1892 + 170.5] = 71.2 \text{ Btu}\end{aligned}$$

$$mc_v = 4.385 + 0.000886T$$

From Eq. (18:2),

$$\begin{aligned}u_2 - u_1 &= \frac{1}{28.96} \int_{500}^{797} (4.385 + 0.000886T) dT = \left( \frac{1}{28.96} \right) [4.385T + 0.000443T^2] \\ &= \left( \frac{1}{28.96} \right) [1307 + 170.5] = 51.0 \text{ Btu}\end{aligned}$$

From Eq. (18:4),

$$\begin{aligned}s_2 - s_1 &= \frac{1}{28.96} \int_{500}^{797} \frac{(6.37 + 0.000886T) dT}{T} - \frac{53.3}{778} \log_e \frac{75}{14.7} \\ &= \frac{6.37}{28.96} \log_e \frac{797}{500} + \frac{(0.000886)(297)}{28.96} - (0.0685)(1.63) = 0.103 + 0.009 \\ &\quad - 0.112 \\ &= 0 \text{ (isentropic)}\end{aligned}$$

$${}_1W_2 = J(u_1 - u_2) = (778)(-51.0) = -39,700 \text{ ft-lb}$$

$$(b) \quad T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{(k-1)/k} = 500 \left( \frac{75}{14.7} \right)^{0.288} = 799^\circ\text{R}$$

$$h_2 - h_1 = 0.24(799 - 500) = 71.7 \text{ Btu}$$

$$u_2 - u_1 = (0.171)(299) = 51.2 \text{ Btu}$$

$$s_2 - s_1 = 0$$

$${}_1W_2 = (778)(-51.2) = -39,800 \text{ ft-lb}$$



The discrepancy between the two sets of results averages less than 1 per cent. However, if the temperature range had extended into the higher temperatures the difference would have been greater.

**18:3. The Gas Tables.** Many engineering problems are concerned with the expansion or the compression of gases. The gas tables<sup>1</sup> make less tedious the solution of these problems by compiling the properties of air, of the products of combustion of a hydrocarbon of formula (CH<sub>2</sub>)<sub>n</sub> with 400 and 200 per cent excess air,<sup>2</sup> of nitrogen, oxygen, water vapor, carbon dioxide, hydrogen, and carbon monoxide in a form designed to be of greatest advantage to the engineer in making the usual class of computations.

The basic assumption in the compilation of the gas tables is that the gases are, at low pressures,<sup>3</sup> perfect gases with variable specific heat. The equation for the specific heat is based on spectroscopic data; it is a more

TABLE 18:2. AIR AT LOW PRESSURES\*

<i>T</i>	<i>t</i>	<i>h</i>	<i>p<sub>r</sub></i>	<i>u</i>	<i>v<sub>r</sub></i>	<i>φ</i>
300	−159.7	71.61	0.17795	51.04	624.5	0.46007
400	−59.7	95.53	0.4858	68.11	305.0	0.52890
500	40.3	119.48	1.0590	85.20	174.90	0.58233
520	60.3	124.27	1.2147	88.62	158.58	0.59173
540	80.3	129.06	1.3860	92.04	144.32	0.60078
560	100.3	133.86	1.5742	95.47	131.78	0.60950
600	140.3	143.47	2.0050	102.34	110.88	0.62607
700	240.3	167.56	3.446	119.58	75.25	0.66321
795	335.3	190.59	5.404	136.09	54.49	0.69405
800	340.3	191.81	5.526	136.97	53.63	0.69558
868	408.3	208.41	7.389	148.91	43.51	0.71550
900	440.3	216.26	8.411	154.57	39.64	0.72438
1000	540.3	240.98	12.298	172.43	30.12	0.75042
1500	1040.3	369.17	55.86	266.34	9.948	0.85416
2000	1540.3	504.71	174.00	367.61	4.258	0.93205
3000	2540.3	790.68	941.4	585.04	1.1803	1.04779
4000	3540.3	1088.26	3280	814.06	0.4518	1.13334
5000	4540.3	1392.87	8837	1050.12	0.20959	1.20129
6000	5540.3	1702.29	20120	1291.00	0.11047	1.25769

\* Abstracted by permission from Table 1, "Gas Tables" by J. H. Keenan and J. Kaye, John Wiley & Sons, Inc., New York, 1948.<sup>1</sup>

<sup>1</sup> J. H. Keenan and J. Kaye, "Gas Tables," John Wiley & Sons, Inc., New York, 1948.

<sup>2</sup> See Art. 19:2.

<sup>3</sup> Low pressures are assumed to include the pressures normally encountered in the engineering process. The error of the air table, at 32°F, is about 1 per cent at 300 psia; it is less at lower pressures or higher temperatures. For gases with higher critical temperatures than air, the error is greater than for air at the same pressure and temperature.

accurate and more complicated expression than the engineer would be apt to choose for his purpose if he were required to make the necessary detailed computations himself. The tables are keyed by absolute temperature in degrees Rankine and cover various ranges according to the gas; the range for the air table is 100 to 6500°R. The base temperature, at which the enthalpy is zero, is 0°R. Since the product  $PV$  is zero at this temperature, the internal energy is also zero. The properties of air are given with respect to 1 lb, for the other gases in terms of the mole.

An abstract from Table 1 of the gas tables, the air table, is presented here by permission as the basis of a discussion of the method of use of the tables, all of which are similarly arranged; it is Table 18:2.

The enthalpy is tabulated in the third column of the air table. It has been computed by applying Eq. (18:1) with  $h_1 = 0$  at 0°R, or

$$h = \int_0^T c_p dT \quad (18:6)$$

The fourth column tabulates values of the relative pressure  $p_r$ . When the values of  $p_r$  are compared at two temperatures, they furnish a key to the pressure ratio in an isentropic process between the limiting temperatures. Thus, denoting the two temperature levels by the subscripts 1 and 2,

$$\left( \frac{p_1}{p_2} \right)_s = \frac{p_{r1}}{p_{r2}} \quad (18:7)$$

The fifth column of the air table lists values of the internal energy. Since  $u = h - Pv/J = h - RT/J$ , the internal energy may be readily calculated from the enthalpy but is here tabulated for convenience.

Values of the relative volume  $v_r$  are tabulated in the sixth column. As was the case with  $p_r$ , the ratio of the values of  $v_r$  at any two temperatures equals the ratio between the volumes at the ends of an isentropic that connects the two temperatures, or

$$\left( \frac{V_1}{V_2} \right)_s = \frac{v_{r1}}{v_{r2}} \quad (18:7a)$$

Any value may be arbitrarily assigned to either  $p_r$  or  $v_r$  at any one temperature, the values at all other temperatures being based upon the selection which is decided upon. The values which are assigned in the air table are such that at each temperature  $v_r$  is numerically equal to the volume of 1 lb, in cubic feet per pound, at the pressure  $p_r$ , in psia. The relation between  $v_r$  and  $p_r$  is therefore  $v_r = 53.3T/144p_r$ .

The last column of the air table gives values of

$$\phi = \int_0^T \frac{c_p dT}{T} \quad (18:8)$$



This quantity, it will be noted, is also a property that is a function of the temperature alone; its value is zero at the base temperature of 0°R. From Eq. (18:14),

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - \frac{R}{J} \log_e \frac{p_2}{p_1} = \phi_2 - \phi_1 - \frac{R}{J} \log_e \frac{p_2}{p_1} \quad (18:9)$$

The tables of properties of the other gases differ from the air table only in that  $h$ ,  $u$ , and  $\phi$  are stated for 1 mole instead of 1 lb and that  $v_r$  is the volume in cubic feet per mole at the pressure  $p_r$ , so that  $v_r = 1545T/144p_r$ . This change is convenient in dealing with hydrocarbons and the products of their combustion since it makes it possible for a single table to serve for a whole series of hydrocarbons.

The data of the gas tables may be applied to good effect in calculations concerned with any of the types of processes discussed in Art. 18:2 since  $\Delta h$  may be substituted for  $\int_{T_1}^{T_2} c_p dT$ ,  $\Delta u$  for  $\int_{T_1}^{T_2} c_v dT$ , and  $\Delta\phi$  for  $\int_{T_1}^{T_2} \frac{c_p dT}{T}$ . A great deal of additional information is also tabulated in the gas tables; some of this concerns other properties, such as the coefficient of viscosity, and some is concerned with smoothing the path of the engineer in special calculations, such as the plotting of Fanno and Rayleigh lines. Two simple examples of the application of the air table to the solution of an engineering problem are given below.

*Example 18:3A.* Solve Example 18:2, using the air table.

*Solution.* At  $T_1 = 500^\circ\text{R}$  read  $p_{r_1} = 1.0590$ . Then  $p_{r_2} = (75/14.7)(1.0590) = 5.40$ . This corresponds, closely, to the tabulated value of  $p_r$  at  $T_2 = 795^\circ\text{R}$ . The change of enthalpy is the difference between the tabulated values of the enthalpy at  $795^\circ\text{R}$  and  $500^\circ\text{R}$ , or

$$h_2 - h_1 = 190.59 - 119.48 = 71.11 \text{ Btu}$$

Using the tabulated values of the internal energy,

$$u_2 - u_1 = 136.09 - 85.20 = 50.89 \text{ Btu}$$

Checking the change of entropy, which should be zero for this isentropic process,

$$s_2 - s_1 = \phi_2 - \phi_1 - \frac{R}{J} \log_e \frac{p_2}{p_1} = 0.69405 - 0.58233 - \left( \frac{53.3}{778} \right) (1.63) = 0$$

Also,

$${}_1W_2 = (778)(-50.89) = -39,600 \text{ ft-lb}$$

Checking the ratio of the tabulated values of  $v_r$ ,  $v_{r_1} = 174.90$ , and  $v_{r_2} = 54.59$ . Therefore

$$\frac{v_2}{v_1} = \frac{v_{r_2}}{v_{r_1}} = \frac{54.49}{174.90} = 0.312$$

From  $Pv = RT$ ,

$$v_2 = \frac{(53.3)(795)}{(75)(144)} = 3.93 \text{ ft}^3/\text{lb}$$

$$v_1 = \frac{(53.3)(500)}{(14.7)(144)} = 12.6 \text{ ft}^3/\text{lb}$$

and

$$\frac{v_2}{v_1} = \frac{3.93}{12.6} = 0.312$$

*Example 18:3B.* Air is compressed adiabatically from 14.7 psia, 40°F, to  $p_2 = 75$  psia in an axial-flow compressor with an efficiency (see Art. 11:15) of 80 per cent. Based on the air table, find the final temperature and the work of compression per pound of air compressed.

*Solution.* The actual change of enthalpy is, according to the definition of compressor efficiency given in Art. 11:15, equal to the isentropic change of enthalpy between the initial state and the final pressure, divided by the efficiency. The isentropic change of enthalpy has been shown in Example 18:3A to be 71.11 Btu. Then

$$h_2 - h_1 = \frac{71.11}{0.80} = 88.9 \text{ Btu and } h_2 = h_1 + 88.9 = 208.38 \text{ Btu}$$

This enthalpy corresponds, according to the air table, to a temperature  $T_2 = 868^\circ\text{R}$ . The work of compression for this adiabatic steady-flow process is

$${}_1W_2 = J(h_1 - h_2) = (778)(-88.9) = -69,200 \text{ ft-lb/lb}$$

**18:4. The van der Waals Equation.** Based on the equation of state of a perfect gas, the pressure

$$P = \frac{RT}{v}$$

The concept of a perfect gas (see Art. 9:2) is of a hypothetical substance the molecules of which are so far apart that intermolecular collisions do not occur and attractive forces between molecules vanish; consistent with these two assumptions, we find that the perfect-gas relation holds with greater accuracy at lower pressures and, consequently, larger volumes.

The effect of intermolecular collision is to cause a given molecule to strike the walls of the container more frequently and thus, when the total effect of the bombardment of all the molecules is considered, to increase the pressure on those walls. In 1873, van der Waals advanced the theory that the pressure would, owing to this effect, be increased in inverse proportion to the ratio of the net volume, obtained by subtracting the actual volume of all the individual molecules from the total space occupied by the gas, to the total volume which the gas fills. As the gas nears the dense liquid phase, this ratio approaches a minimum and the increase of pressure due to this effect a corresponding maximum.

The effect of the attractive forces between molecules is, in the limit as the liquid phase is approached, to cause the molecules to cling together;



the outward pressure exerted against the walls of a container is reduced. Van der Waals suggested that the pressure of the gas would be reduced, because of this effect, in proportion to the square of its density and proposed the following equation to reflect both effects in altering the pressure,

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad (18:10)$$

in which  $a$  and  $b$  are dimensional constants. The constant  $b$  represents the volume actually occupied by the molecules of the substance, and its size is therefore of the order of the specific volume of the fluid in its liquid phase, with the molecules closely packed together;  $v - b$  is correspondingly the net volume to which reference has been made above. At low pressures,  $v$  is large, and  $v - b$  approaches  $v$  in magnitude; as a result the  $RT/(v - b)$  term approaches in value the pressure as determined from the perfect-gas relation. The constant  $a$  is a proportionality constant which reflects the effect of density in reducing the pressure by accounting for an increase in the attractive forces between molecules. At low pressures,  $v^2$  becomes very large and the reduction of pressure represented by the  $a/v^2$  term correspondingly small. Thus the van der Waals equation approaches the perfect-gas relation at low pressures.

The van der Waals equation may be easily solved for pressure when the values of the constants and of the temperature and volume are known. In the form

$$RT = \left( P + \frac{a}{v^2} \right) (v - b) \quad (18:11)$$

it may be as readily solved for temperature; for volume alone it is not explicit. With known values of  $a$  and  $b$ , Eq. (18:10) may be used to plot the family of isothermals shown in Fig. 18:1. Below a certain temperature  $T_c$ , these isothermals will be observed to have three real roots in  $v$  in a fixed range of pressures (for the isothermal  $T = T_1$ , within the range  $P_h$  to  $P_j$ ). Above  $T_c$  there is only a single real root for every value of  $P$ , and the curve ( $T = T_3$ ) has a negative slope throughout while, at  $T_c$ , the isothermal, although it has everywhere only a single root in  $v$ , is instan-

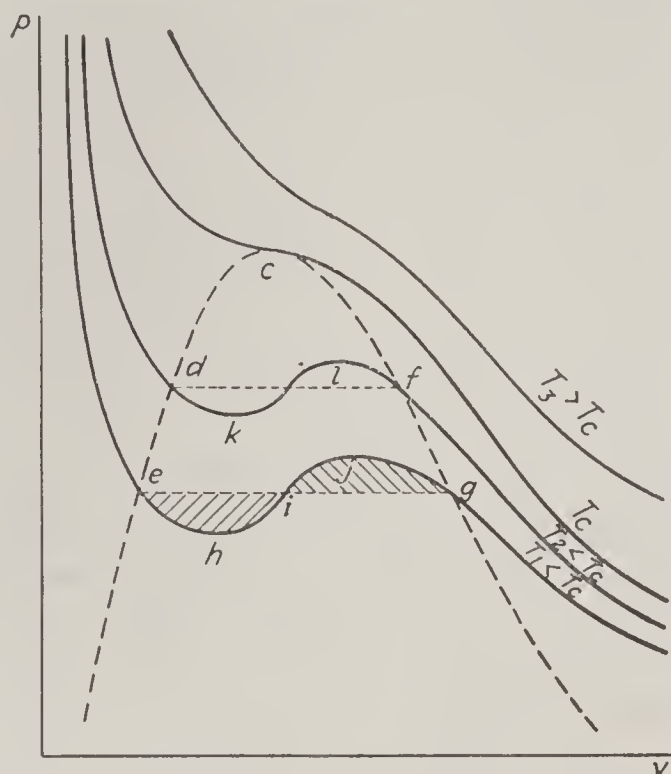


FIG. 18:1. The van der Waals equation of state.

taneously horizontal at  $c$ . If the points  $e, d, c, f$ , and  $g$  are now connected, as by the dashed line of the figure, the resemblance to the line  $aimgnjc$  of Fig. 7:3 is noteworthy. On Fig. 7:3 this line connects saturated-liquid and saturated-vapor states on a pressure-volume diagram.

The resemblance of isothermal  $T_3$  of Fig. 18:1 to isothermal  $rs$  of Fig. 7:3 is marked, as is that of isothermal  $T_c$  of Fig. 18:1 to the isothermal at the critical temperature in Fig. 7:3. Below  $T_c$  the isothermals of the two figures are also similar in appearance except in the two-phase region between the saturated-liquid and saturated-vapor lines. In this space, the isothermal of the substance that is in stable equilibrium becomes horizontal while the van der Waals isothermal is a rising and falling curve. The dotted line  $eig$  has been added on Fig. 18:1 to represent the state path followed by the two-phase fluid when the temperature is constant; the constant pressure along this path is the saturation pressure equivalent to the temperature  $T_1$ .

With reference to Fig. 18:1, points along the path segment  $eh$  represent states at which the pressure of the liquid is less than the saturation pressure equivalent to its temperature. These are metastable states that may be observed experimentally under laboratory conditions; the liquid is said to be *superheated*. Similarly, the path segment  $gj$  passes through states at which the temperature of the vapor is below the saturation temperature corresponding to its pressure; this class of metastable states is often observed in the flow of steam through nozzles and has been discussed in Art. 11:8. On the other hand, states along the path segment  $hij$ , where  $\left(\frac{\partial P}{\partial V}\right)_T > 0$ , may be shown, by methods which are beyond the scope of this text, to be unstable; they will not exist long enough to be observed.

The purpose of the preceding paragraph has been to indicate that the undulating curve of the van der Waals isothermal as it crosses the two-phase region, although it does not connect states of stable equilibrium, may be interpreted in part in terms of observable states of the real fluid. In locating the stable-equilibrium line  $eig$  across the two-phase region, it is observed that this line is a line of constant pressure and of constant temperature. A cycle may be reversibly traversed by following the path  $ehijgie$ , and, during this cycle, the temperature has remained constant. According to the Second Law, no net work could have resulted, and area  $eih$  must therefore be equal to area  $ijg$ .

An obvious point of coincidence between Figs. 7:3 and 18:1 is the point  $c$  at which the isothermal  $T_c$  of Fig. 18:1 becomes instantaneously horizontal; this corresponds to the critical point  $g$  of Fig. 7:3. For many real fluids the critical pressure, temperature, and volume have been determined, even though their equations of state have not been derived, and



this critical state can be made the basis of the selection of the values of the constants  $a$  and  $b$  of the van der Waals equation when that equation is to be fitted to a particular substance.

If the first derivative of the van der Waals equation is placed equal to zero, the result will be the equation of the line which passes through the minima and maxima of the family of isothermals pictured in Fig. 18:1 (connecting points such as  $h$ ,  $k$ ,  $c$ ,  $l$ , and  $j$ ). Thus

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

(18:12)

is the equation of this line. The maximum on the curve represented by this equation occurs at critical point  $c$  and may be located by taking the first derivative of Eq. (18:12), which is the second derivative of the van der Waals equation, and equating it to zero, or

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

(18:13)

But point  $c$  satisfies both Eq. (18:12) and Eq. (18:13) and, solving them simultaneously,

$$v_c = 3b$$

(18:14)

$$T_c = \frac{8a}{27bR}$$

(18:15)

Substituting in Eq. (18:10),

$$P_c = \frac{a}{27b^2}$$

(18:16)

TABLE 18:3. CRITICAL CONSTANTS\*

No.	Gas	Sym- bol	Mol. wt	$R$ , ft/°R	$T_c$ , °R	$p_c$ , psia	$v_c$ , ft <sup>3</sup> /lb	$Z_c$ $P_c v_c / RT_c$
1	Oxygen	O <sub>2</sub>	32.00	48.3	278	730	0.0372	0.292
2	Nitrogen	N <sub>2</sub>	28.02	55.2	227	492	0.0515	0.292
3	Air	....	28.96	53.3	238	547	0.0470	0.292
4	Hydrogen	H <sub>2</sub>	2.016	766	60	188	0.517	0.305
5	Carbon dioxide	CO <sub>2</sub>	44.00	35.1	548	1073	0.0348	0.279
6	Carbon monoxide	CO	28.00	55.2	241	508	0.0515	0.283
7	Water	H <sub>2</sub> O	18.02	85.8	1165	3206	0.0503	0.232
8	Methane	CH <sub>4</sub>	16.03	96.4	344	673	0.0989	0.289
9	Ethylene	C <sub>2</sub> H <sub>4</sub>	28.03	55.1	509	747	0.0728	0.279
10	Ethane	C <sub>2</sub> H <sub>6</sub>	30.05	51.4	550	708	0.0763	0.275
11	Octane	C <sub>8</sub> H <sub>18</sub>	114.1	13.5	1025	362	0.069	0.260

\* Data from various sources, including International Critical Tables, and *Natl. Bur. Standards (U.S.) Circ. 279* (December, 1925).

The ratio  $Pv/RT$  is called the *compressibility factor* and is denoted as  $Z$ . For the perfect gas, it has the constant value of 1; for real gases it is not a constant but is a function of both temperature and pressure. At the critical point the value of the compressibility factor is

$$Z_c = \frac{P_c v_c}{RT_c} \quad (18:17)$$

When the values of the critical volume, temperature, and pressure from Eqs. (18:14) to (18:16) are substituted in Eq. (18:17), it is discovered that the van der Waals equation gives a value of  $Z_c = \frac{3}{8}$ . In Table 18:3 are presented critical-state data for a number of substances. It is immediately observed that  $Z_c$  for all these substances is well below the value of  $\frac{3}{8}$  which is obtained for that ratio from the van der Waals equation, and it appears that the application of the equation at states close to the critical point will result in errors of the order of 10 to 40 per cent.<sup>1</sup>

In spite of its lack of accuracy, the van der Waals equation is of considerable interest and importance because:

1. It illustrates a rational method of attacking the problem of setting up a general equation of state.
2. Its lines of constant temperature, even in the two-phase region where they seem to be widely different from the isothermals of a vapor, may be interpreted in terms of the behavior of the real substance.
3. It covers all fluid regions, from the compressed liquid to the gas, and shows the general characteristics of the real substance, even though it does not give precise values of the properties.

No single general equation of state is known which represents the properties of all fluid phases with precision. Assuming that such an equation is developed, it is highly probable that it will be of such complexity as to be of little practical use to the engineer.

The critical pressure and temperature can be more easily and accurately measured than can the critical volume. For this reason, although Eq. (18:14) can be readily solved for  $b$  in terms of  $v_c$ , it is better to express its value in terms of  $T_c$  and  $P_c$ ; the same is true of the constant  $a$ . Thus, from Eq. (18:16),

$$a = 27b^2P_c \quad (18:18)$$

<sup>1</sup> The van der Waals equation can be made to give a better fit for states near the critical state by assigning an artificial value to  $R$  such that Eq. (18-17) will yield the compressibility factor that is characteristic of the particular substance at its critical state. However, when this is done, the equation loses accuracy when applied to other areas. For example, at low pressures it no longer approximates the perfect-gas relation, which is known to hold closely in that region.



and, substituting this value in Eq. (18:15),

$$T_c = \frac{8bP_c}{R}$$

or

$$b = \frac{RT_c}{8P_c} \quad (18:19)$$

Substituting this value of  $b$  in Eq. (18:18),

$$a = \frac{27R^2T_c^2}{64P_c} \quad (18:20)$$

*Example 18:4.* Using the van der Waals equation, calculate, for water, the pressure corresponding to temperature-volume conditions  $a$ ,  $b$ , and  $c$ , as given below. At the calculated pressure and the given temperature, read the volume from the steam tables and compare with the given volume, finding the error percentage. (a)  $t = 1200^\circ\text{F}$ ;  $v = 0.24 \text{ ft}^3/\text{lb}$ . (b)  $t = 720^\circ\text{F}$ ;  $v = 0.17 \text{ ft}^3/\text{lb}$ . (c)  $t = 500^\circ\text{F}$ ;  $v = 40 \text{ ft}^3/\text{lb}$ .

*Solution:*

(a) From Eq. (18:19),

$$b = \frac{(85.8)(1165)}{(8)(3206)(144)} = 0.0271 \text{ ft}^3/\text{lb}$$

From Eq. (18:20),

$$a = \frac{(27)(85.8)^2(1165^2)}{(64)(3206)(144)} = 9130 \frac{(\text{psf})(\text{ft}^6)}{\text{lb}^2}$$

Substituting  $T_a$  and  $v_a$  in Eq. (18:10),

$$P_a = \frac{(85.8)(1660)}{0.24 - 0.0271} - \frac{9130}{0.24^2} = 669,000 - 158,500 = 510,500 \text{ psf} = 3540 \text{ psia}$$

At this pressure and the temperature of  $1200^\circ\text{F}$ , the steam tables give the specific volume as 0.2514. At this state the van der Waals equation gives too low a volume by about 5 per cent.

$$(b) P_b = \frac{(85.8)(1180)}{0.17 - 0.0271} - \frac{9130}{0.17^2} = 708,000 - 316,000 = 392,000 \text{ psf} = 2720 \text{ psia}$$

The steam-table value for the volume at this pressure and a temperature of  $720^\circ\text{F}$  is 0.1569. The van der Waals equation gives a volume that is too high by about 9 per cent.

$$(c) P_c = \frac{(85.8)(960)}{40 - 0.0271} - \frac{9130}{40^2} = 2040 - 6 = 2034 \text{ psf} = 14.1 \text{ psia}$$

At  $p = 14.1 \text{ psia}$ ,  $t = 500^\circ\text{F}$ , the steam tables give a specific volume of  $40.44 \text{ ft}^3$ . The van der Waals volume is about 1 per cent low.

States  $a$ ,  $b$ , and  $c$  in this example have been chosen to illustrate the relative accuracy to be expected from the use of the van der Waals equation in, respectively, the high-pressure high-temperature range, the range of states close to the critical point, and

the low-pressure area. The calculations above indicate, as was to be expected, that the region to which it applies with the least accuracy is in the neighborhood of the critical state. Exactly at the critical state the van der Waals equation gives a volume which is  $0.375/0.232 - 1 = 0.62$ , or 62 per cent too high.

**18:5. Other General Equations of State.** A number of general equations of state have been proposed, some of which follow the van der Waals equation in basing their development on the kinetic theory of gases while others are empirically derived to agree with observed data. Only a few will be discussed here.

1. *The Dieterici equation* was first proposed in 1899. It gives a value of  $Z_c = 0.27$ , a better average value for real gases than the 0.375 of the van der Waals equation. According to this equation in its revised form

$$P = \frac{RT}{v - b} e^{\frac{-a}{T^{1.27}v}} \quad (18:21)$$

with  $a = 4RT_c^{2.27}/P_c e^2$  and  $b = RT_c/P_c e^2$ ;  $e$  is the natural logarithmic base.

*Example 18:5A.* Apply the Dieterici equation to water at the states suggested in Example 18:4, and determine the deviation from steam-table volumes as in that example.

*Solution:*

$$b = \frac{(85.8)(1165)}{(3206)(144)(2.718)^2} = 0.0294$$

$$a = \frac{(4)(85.8)(1165)^{2.27}}{(3206)(144)(2.718)^2} = 916$$

$$(a) \ P_a = \frac{(85.8)(1660)}{0.24 - 0.0294} e^{\frac{-916}{(1660^{1.27})(0.24)}} = 676,000e^{-0.313} = 495,000 \text{ psf} = 3440 \text{ psia}$$

At  $p = 3440$ ,  $t = 1200$ , the steam tables give a volume of 0.2596. The Dieterici volume is about 7 per cent too low.

$$(b) \ P_b = \frac{(85.8)(1180)}{0.17 - 0.0294} e^{\frac{-916}{(1180^{1.27})(0.17)}} = 720,000e^{-0.677} = 366,000 \text{ psf} = 2540 \text{ psia}$$

At  $p = 2540$ ,  $t = 720$ , the steam-table volume is 0.179. The Dieterici volume is in error by about 5 per cent.

$$(c) \ P_c = \frac{(85.8)(960)}{40 - 0.0294} e^{\frac{-916}{(1180^{1.27})(40)}} = 2062e^{-0.0037} = 2055 \text{ psf} = 14.27 \text{ psia}$$

The steam tables give  $v = 39.98$  at  $p = 14.27$ ,  $t = 500$ . This agrees almost exactly with the Dieterici volume.

2. *The Berthelot equation*, proposed in 1903, resembles the van der Waals equation and gives the same value of  $Z_c$  as that equation. It is suitable



for use at states having temperatures well above the critical temperature.

$$P = \frac{RT}{v - b} - \frac{a}{Tv^2}$$

(18:22)

with  $a = 27R^2T_c^3/64P_c$  and  $b = RT_c/8P_c$ .

3. *The Beattie-Bridgman equation* (1928) is an example of an equation that has been devised to fit observed experimental data. Its constants cannot be evaluated from critical-state data alone but must be taken from tables which give their value for specific gases. It therefore cannot be classified with the van der Waals, Dieterici, and Berthelot equations as an entirely general equation of state. On the other hand, as would be expected, it is the most accurate of the four in the range in which its use is recommended; it should not be used when the specific volume is less than twice the critical specific volume. The equation is stated as

$$P = \frac{mRT(1 - \epsilon)}{m^2v^2} (mv + B) - \frac{A}{m^2v^2}$$

(18:23)

TABLE 18:4.    CONSTANTS FOR BEATTIE-BRIDGMAN EQUATION OF STATE\*

No	Gas	Symbol	$A_0,$ (psf)(ft <sup>6</sup> ) mole <sup>2</sup>	$a,$ ft <sup>3</sup> mole	$B_0,$ ft <sup>3</sup> mole	$b,$ ft <sup>3</sup> mole	$c \times 10^{-6}$ (ft <sup>3</sup> )(°R) <sup>3</sup> mole
1	Oxygen	O <sub>2</sub>	808,000	0.410	0.740	0.067	4.48
2	Nitrogen	N <sub>2</sub>	730,000	0.419	0.808	−0.111	3.92
3	Hydrogen	H <sub>2</sub>	107,000	−0.081	0.336	−0.698	0.0471
4	Carbon dioxide	CO <sub>2</sub>	2,720,000	1.143	1.678	1.159	61.65
5	Carbon monoxide	CO	729,000	0.419	0.808	−0.111	3.92
6	Methane	CH <sub>4</sub>	1,236,000	0.297	0.894	−0.254	11.98
7	Ethylene	C <sub>2</sub> H <sub>4</sub>	3,330,000	0.794	1.945	0.575	21.18
8	Ethane	C <sub>2</sub> H <sub>6</sub>	3,190,000	0.938	1.504	0.306	84.20

\* From *Proc. Am. Acad. Arts Sci.*, **63**, 64 (1928–1930).

where  $A = A_0 \left(1 - \frac{a}{mv}\right)$ ,  $B = B_0 \left(1 - \frac{b}{mv}\right)$ ,  $\epsilon = \frac{c}{mvT^3}$ , and  $A_0$ ,  $a$ ,  $B_0$ ,  $b$ , and  $c$  are constants having different values for each gas. Table 18:4 gives their values for a few substances. In this equation  $m$  is the molecular weight,  $mv$  being the molar volume and  $mR$  the universal gas constant.

*Example 18:5B.* Using the Beattie-Bridgman equation, calculate the pressure that corresponds, for carbon dioxide, to a temperature of 250°F and a specific volume of 0.2 ft<sup>3</sup>/lb. Using the calculated pressure, determine the value of  $Z$ , the compressibility factor.

*Solution.* From Eq. (18:23), using the constants for CO<sub>2</sub> from Table 18:4,

$$A = 2,720,000 \left[ 1 - \frac{1.143}{(44)(0.2)} \right] = 2,350,000$$

$$B = 1.678 \left[ 1 - \frac{1.159}{(44)(0.2)} \right] = 1.457$$

$$\epsilon = \frac{61,650,000}{(44)(0.2)(710)^3} = 0.0196$$

$$mv = (44)(0.2) = 8.8$$

$$P = \frac{(1545)(710)(1 - 0.0196)(8.8 + 1.457) - 2,350,000}{8.8^2} = 112,500 \text{ psf} = 780 \text{ psia}$$

$$Z = \frac{Pv}{RT} = \frac{(780)(144)(0.2)}{(35.1)(710)} = 0.90$$

4. For none of the foregoing equations, including the equation of van der Waals, is the volume an explicit function. Since the pressure and the temperature are the properties most readily and most accurately measurable, an expression for which  $v$  is the dependent variable is desirable. Such an equation is

$$v = \frac{RT}{P} (1 + \alpha_1 P + \Sigma \alpha_i P^i) \quad (18:24)$$

in which  $\Sigma \alpha_i P^i$  represents a series of terms in each of which  $\alpha$  is, as is  $\alpha_1$ , a function of temperature alone and the exponent  $i$  is in each term greater than 1. It is usual, though not necessary, to use integer powers of  $P$ . A formula of this type has been used in the preparation of the Keenan and Keyes steam tables.<sup>1</sup> It will be observed that at zero pressure a value of  $Z = 1$  will result, as for the perfect gas and all of the general equations of state discussed above.

By mathematical manipulation, many equations of state for which  $P$  is the dependent variable may be closely approximated in the often more convenient form in which  $v$  is explicit; a series results which follows Eq. (18:24) in its form.<sup>2</sup>

**18:6. The law of corresponding states** was proposed to meet the situation where detailed information, with the exception of the values of the pressure, temperature, and volume at the critical state, in regard to a particular substance is lacking but a fairly close approximation of its properties is acceptable. The law is based on the premise that the  $PvT$  surfaces (see Fig. 7:1) of all substances are geometrically similar, and may be stated in mathematical terms as

$$V_R = f(P_R, T_R) \quad (18:25)$$

<sup>1</sup> See J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," equation (13), p. 15, John Wiley & Sons, Inc., New York, 1936.

<sup>2</sup> For an application of this principle to the Beattie-Bridgman equation, see J. H. Keenan, "Thermodynamics," John Wiley & Sons, Inc., 1941.



in which  $V_R$ ,  $P_R$ , and  $T_R$  are the reduced values of the corresponding properties, *i.e.*, the ratio of their values to the value of the corresponding property at the critical state. Thus  $V_R = v/v_c$ ,  $P_R = P/P_c$ , and  $T_R = T/T_c$ . If two fluids have the same value of  $V_R$ ,  $P_R$ , and  $T_R$ , they are in corresponding states.

In making use of this law, when it is desired to determine the volume at some state where the pressure and temperature are, respectively,  $P$  and  $T$ , the values of the ratios  $P_R$  and  $T_R$  are computed. These ratios are then carried to a chart or table which shows the  $P$ ,  $T$ , and  $v$  relations for some second substance, whose properties are known with a high degree of precision, and the corresponding state is located. At that state the volume is obtained and compared with  $v_c$  for this reference substance. This gives  $V_R$ , and this ratio may now be carried back and used in connection with  $v_c$  for the first substance to obtain its volume at the stated pressure and temperature.

The law of corresponding states is not suitable for use at low pressures where all gases obey the perfect-gas relation. For the law assumes that the values of  $Z$ , the compressibility factor, for the two gases at corresponding states will always be in the ratio of the values of this factor at their respective critical states. At zero pressure  $Z = 1$  for all gases, and, for the law to hold, it would be required that the ratio  $Z_{c1}/Z_{c2}$ , where the subscripts 1 and 2 refer to the two gases that are being compared, must be 1. In Table 18:3 it is shown that all gases do not have the same ratio  $Z_c$ , the variation being from about 0.2 to 0.3. The law gives fairly accurate results when used for states near the critical state; it is also used in the range where  $T_R$  and  $P_R$  are greater than 1. Figure 18:2 presents a chart which may be used for this purpose; it shows the reduced isometrics on a graph for which  $P_R$  is the ordinate and  $T_R$  the abscissa. The isometrics shown on this chart are average curves for a number of gases, all of which have values of  $Z_c$  in the vicinity of 0.28.

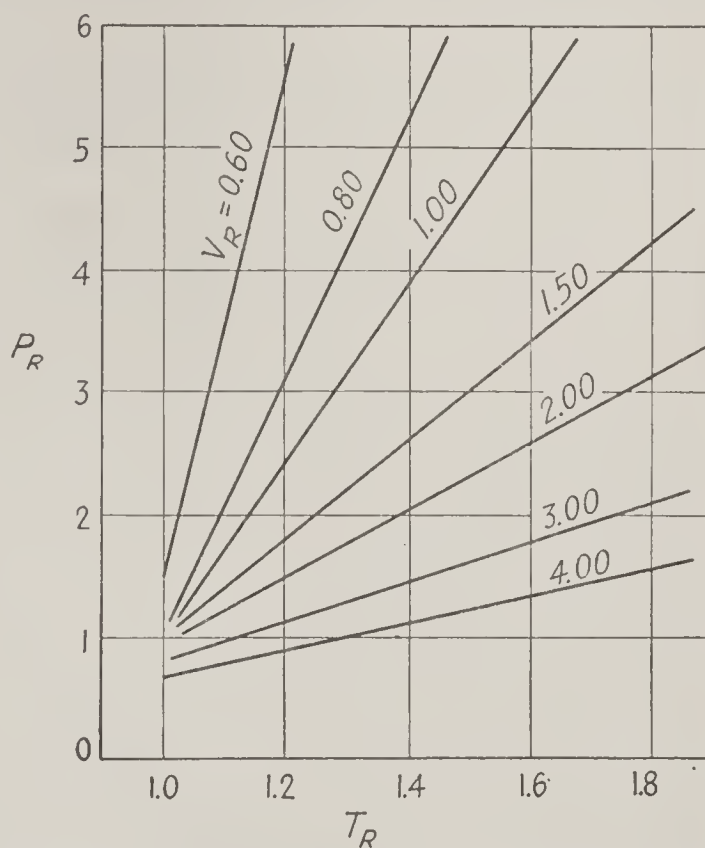


FIG. 18:2. The law of corresponding states. (From thesis by W. C. Kay, Massachusetts Institute of Technology, 1937.)

**18:7. The Generalized  $Z$  Chart.** The relation between  $Z$  and the reduced pressure is similar for different substances, and this similarity

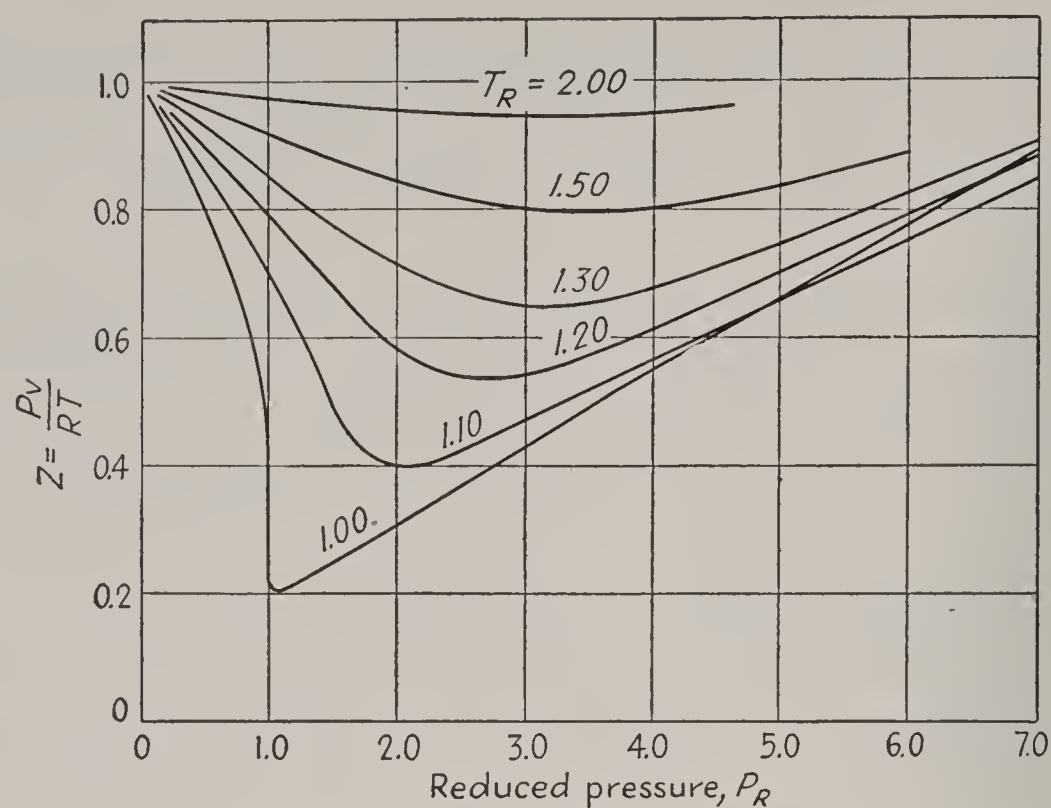


FIG. 18:3. Generalized compressibility factor—reduced pressure chart. [Adapted from Gonq-Jen Su, "Modified Law of Corresponding States for Real Gases," *Ind. Eng. Chem.*, **38** (August, 1946).]

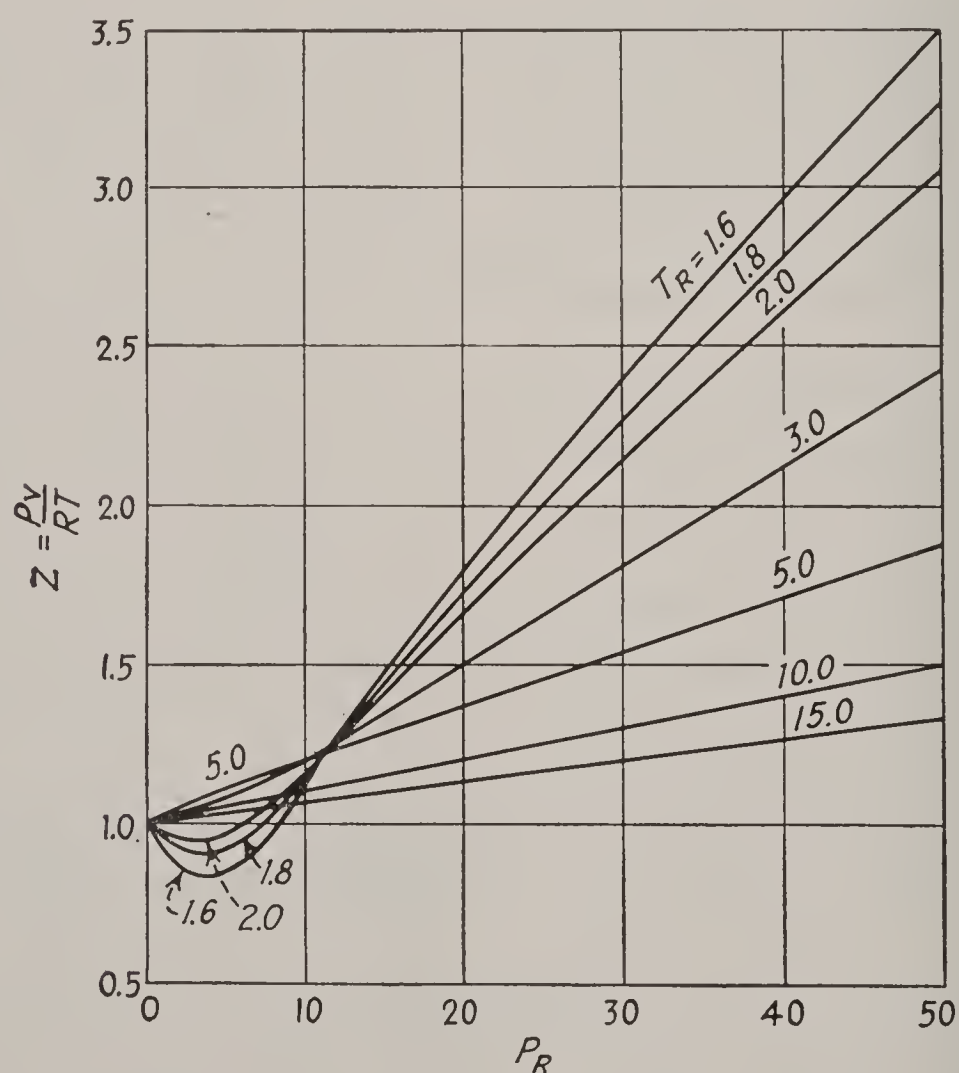


FIG. 18:4. Z chart for high ranges. (Adapted from chart by Weber from data of Gonq-Jen Su, "Thermodynamics for Chemical Engineers," by Harold C. Weber, John Wiley & Sons, Inc., New York, 1939.)



may be used as the basis of an estimate of the volume of a gas when information as to its critical state is available. Generalized charts on which the values of  $Z$  are plotted as ordinates against  $P_R$  as abscissas are shown in Figs. 18:3 and 18:4. In using these charts the values of  $P_R$  and  $T_R$  that correspond with a given state at which it is desired to estimate the volume are calculated, the corresponding point is located on the chart, and the value of  $Z$  is read. This value of  $Z$  may then be used to calculate the volume. It will be observed that this method, although based in general on the law of corresponding states, avoids some of the inaccuracy of that law at low pressure, since all of the reduced isothermals pass through  $Z = 1$  at zero pressure.

*Example 18:7.* Using the generalized  $Z$  charts, check the value of  $Z$  that was calculated in Example 18:5*B*.

*Solution:*

$$P_R = \frac{7.50}{1073} = 0.70; T_R = \frac{7.10}{548} = 1.295$$

This point, when located on Fig. 18:3, gives  $Z = 0.89$ . This compares with  $Z = 0.90$ , as based on the Beattie-Bridgman equation.

**18:8. The Properties of a Real-gas Mixture.** In any mixture of real gases that is in equilibrium, we may write

$$\begin{aligned} T_1 &= T_2 = T_3 = \cdots = T_n = T_m \\ V_1 &= V_2 = V_3 = \cdots = V_n = V_m \\ P_1 + P_2 + P_3 + \cdots + P_n &= P_m \end{aligned}$$

in which the subscripts 1 to  $n$  refer to the components and the subscript  $m$  to the mixture. But the mole fractions of the constituents are not in proportion to their partial pressures in the mixture (see Art. 10:3) unless the pressure of the mixture is low and the mixture can be considered to be composed of perfect gases. At high pressures considerable error is invited in attempting to apply these mixture relations to the problem of approximating the connection between the pressure, volume, and temperature of a real-gas mixture. A number of other methods which seem more promising have been suggested, two of which are briefly discussed below.

1. Kay<sup>1</sup> assumes that the mixture can be treated as a single gas with a critical pressure and a critical temperature that have been obtained by averaging these values for the constituents of the mixture. The psuedo-critical temperature and pressure are based on the following equations,

$$\begin{aligned} T_{c_m} &= x_1 T_{c_1} + x_2 T_{c_2} + x_3 T_{c_3} + \cdots \\ P_{c_m} &= x_1 P_{c_1} + x_2 P_{c_2} + x_3 P_{c_3} + \cdots \end{aligned} \tag{18:26}$$

<sup>1</sup> *Ind. Eng. Chem.*, **28**, 1014 (1936).

in which the subscripts 1, 2, 3, etc., refer to the constituents, the subscript  $m$  to the mixture, and  $x_1, x_2$ , etc., are the respective mole fractions. When the pseudocritical temperature and pressure have been computed, they may be used to find the values of the constants in general equations of state, such as those of van der Waals, Dieterici, or Berthelot, or the generalized  $Z$  chart may be used if only a limited number of states are to be investigated.

An illustration of this method of finding the critical pressure and temperature of a mixture is found in the data for oxygen, nitrogen, and air in Table 18:3. Air is essentially a mixture of oxygen and nitrogen with respective mole fractions equal to about 0.21 and 0.79. When Eqs. (18:26) are applied, the pseudocritical temperature and pressure are calculated as 238°R and 542 psia, checking the tabulated values for air closely.

2. Beattie<sup>1</sup> has proposed that the Beattie-Bridgman equation of state may be used with the constants weighted as follows:

$$\begin{aligned} A_{0_m} &= (x_1 A_{0_1}^{\frac{1}{2}} + x_2 A_{0_2}^{\frac{1}{2}} + x_3 A_{0_3}^{\frac{1}{2}} + \cdots)^2 \\ a_m &= x_1 a_1 + x_2 a_2 + x_3 a_3 + \cdots \\ B_{0_m} &= x_1 B_{0_1} + x_2 B_{0_2} + x_3 B_{0_3} + \cdots \\ b_m &= x_1 b_1 + x_2 b_2 + x_3 b_3 + \cdots \\ c_m &= x_1 c_1 + x_2 c_2 + x_3 c_3 + \cdots \end{aligned} \quad (18:27)$$

This method may be used when the Beattie-Bridgman constants are known for all of the constituents of the mixture and the mass per unit volume of each constituent is less than one-half the critical density of that constituent.

**18:9. Conclusion.** In the foregoing articles of this chapter, methods of developing a  $PvT$  relation for the real gas have been discussed. When this relation has been established, the methods of Art. 8:3 will apply in writing secondary equations of state to express the enthalpy, the internal energy, and the entropy. The van der Waals, Dieterici, Berthelot, and Beattie-Bridgman equations all express the pressure as a function of the temperature and volume. Equations (8:30) to (8:33) illustrate the manner in which these  $PvT$  relations can be used to write the secondary equations for internal energy and for entropy. With the pressure, volume, and internal energy known, Eq. (2:8) may be applied to calculate the enthalpy.

The calculation of internal energy, enthalpy, and entropy is much more convenient when the volume is explicit in the primary equation of state, as in Eq. (18:24). The secondary equations of state then follow Eqs. (8:29) and (8:35) in form.

<sup>1</sup> *J. Am. Chem. Soc.*, **51**, 1929.



## Problems

1. (a) Plot the specific heat at constant pressure per pound of air vs. the temperature in Fahrenheit degrees in the range 260 to 1440°F as based on Eq. (8) of Table 18:1. (b) Plot  $c_v$  for air on the same graph and over the same range. (c) Show  $c_p$  for air on the same graph as based on Eq. (9).

2. Over the temperature ranges that are specified in each case, plot  $c_p$  for hydrogen as based on Eqs. (10) to (13) of Table 18:1 (three curves). Assume a range of 0 to 2000°F for Eq. (11). Compare the three values of  $c_p$  at 1000°F.

3. Table 18:1 is based on the assumption that the perfect-gas relation  $Pv = RT$  may be applied to the gases listed and is therefore limited in its application to comparatively low pressures. Why are no monatomic gases included in the listing?

4. (a) Use Eq. (8) of Table 18:1 in calculating the change of enthalpy per pound of air as the temperature changes from 340 to 1040°F. (b) Calculate the change of internal energy over the same temperature interval. (c) What is the mean value of  $c_p$ ?

5. Based on Eq. (8) of Table 18:1, calculate the change of entropy per pound of air as its temperature changes from 340 to 1040°F and its pressure from 20 to 35 psia.

6. During a reversible process that takes place at constant atmospheric pressure, the temperature of a pound of air decreases from 1040 to 340°F. (a) Based on Eq. (8) of Table 18:1, calculate the heat flow, the external work, and the changes of internal energy and entropy that accompany the process. (b) Repeat as based on Eq. (9) of Table 18:1. (c) Compare the answers to parts *a* and *b* with those which result when  $c_p$  is assumed to be constant at 0.24.

7. During a reversible constant-volume process that begins at atmospheric pressure and a temperature of 340°F, the temperature of 1 lb of air increases to 1040°F. Based on Eq. (8) of Table 18:1, calculate the heat flow, the work, and the changes of internal energy and entropy that accompany the process. Compare with the similar quantities when a constant specific heat (see Table 9:1) is used.

8. At a constant temperature of 340°F, the pressure of an air system decreases from 80 to 20 psia during a reversible process. Equation (8) of Table 18:1 will be assumed to give the variation of specific heat with temperature. Calculate the heat flow, the work, and the changes of internal energy and entropy that accompany the process. Compare with the result when the specific heat is a constant.

9. The reversible adiabatic expansion of a pound of air begins at a pressure of 200 psia and a temperature of 1040°F and ends when the temperature becomes 340°F. (a) Assuming that Eq. (8) of Table 18:1 gives the relation between  $c_p$  and  $T$ , what is the final pressure? What are the initial and final volumes? (b) Calculate the heat flow, the work, and the changes of internal energy and of entropy that accompany the process. (c) What is the mean value of  $k$  as based on the mean values of  $c_p$  and  $c_v$  and as calculated from Eq. (9:28)? (d) Assuming constant specific heats as given in Table 9:1, calculate the heat flow, the work, and the changes of internal energy and of entropy, and compare with the answers to part *b* above.

10. A pound of air is compressed reversibly with  $n = 1.3$  from atmospheric pressure and 340°F until it reaches a temperature of 1040°F. Equation (8) of Table 18:1 will be assumed to represent the relation between  $c_p$  and  $T$ . (a) What are the initial and final volumes and the final pressure? (b) Calculate the heat flow, the work, and the changes of internal energy and of entropy that accompany the process. (c) What is the average value of  $c_n$ , and what are its values at the beginning and at the end of the process? (d) Assuming constant specific heats as given in Table 9:1, calculate the volumes, the final pressure, the heat flow, the work, and the changes of internal energy and of entropy, and compare with the answers to parts *a* and *b*.

11. Solve Prob. 6, using the air table. Compare with the answers to Prob. 6, and explain any discrepancies.
12. Solve Prob. 7, using the air table.
13. Solve Prob. 8, using the air table.
14. Solve Prob. 9, using the air table.
15. Solve Prob. 10, using the air table.
16. In Art. 18:3 it is stated that the gas tables for hydrocarbons are compiled on the basis of 1 mole instead of 1 lb since one table can then serve *for a whole series of hydrocarbons*. How is this possible?
17. For ethylene ( $C_2H_4$ ) calculate the values of the constants  $a$  and  $b$  of the van der Waals equation.
18. Based on the van der Waals equation, calculate the data for, and plot on a  $pv$  diagram, the isothermals for ethylene at 240, 49,  $-160$ , and  $-260^\circ F$ .
19. Show the derivation of Eqs. (18:14) to (18:16) in detail.
20. Show that the compressibility factor at the critical state is  $\frac{3}{8}$  according to the van der Waals equation.
21. At atmospheric pressure, 1 lb of ethylene is found to have a volume of 5 ft<sup>3</sup>. According to the van der Waals equation, what is its temperature? What is the compressibility factor?
22. At a temperature of  $140^\circ F$ , the specific volume of ethylene is 0.23 ft<sup>3</sup>/lb. According to the van der Waals equation, what is its pressure? What is the compressibility factor? Compare with the compressibility factor in Prob. 21, and discuss.
23. Find the volume and pressure coordinates of the maximum and the minimum on the lowest isothermal of Prob. 18.
24. In Prob. 22, what is the pressure as based on (a) the Dieterici equation; (b) the Berthelot equation; (c) the Beattie-Bridgman equation? In each case, what value of  $Z$  applies to the state?
25. According to the Keenan and Keyes tables, the specific volume of steam at a pressure of 5000 psia and a temperature of  $1400^\circ F$  is 0.2027 ft<sup>3</sup>/lb. What are its reduced pressure, reduced temperature, and reduced volume? What is the corresponding state (give pressure, temperature, and specific volume) for ethylene?
26. Using Fig. 18:2 and the data given in Table 18:3, estimate the specific volume of ethylene at 1500 psia and  $350^\circ F$ .
27. Use the generalized  $Z$  charts and the data given in Table 18:3 to estimate the specific volume of ethylene at 1500 psia and  $350^\circ F$ . Compare with the answer to Prob. 26.
28. Use the generalized  $Z$  charts and the data given in Table 18:3 to estimate the specific volume of hydrogen at a pressure of 5000 psia and a temperature of  $80^\circ F$ .
29. A mixture is composed of 0.4 mole fraction of ethylene and 0.6 mole fraction of ethane. (a) Estimate the volume that corresponds to a pressure of 1500 psia and a temperature of  $350^\circ F$  using Kay's method and the generalized  $Z$  charts. (b) Using the Beattie-Bridgman relation, calculate the pressure corresponding to a temperature of  $350^\circ F$  and a specific volume of 0.167 ft<sup>3</sup>/lb.

### Symbols

$a, b, c$	constants
$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$A, B, C, D, E$	constants
$e$	natural logarithmic base
$h$	specific enthalpy
$J$	proportionality factor



$k$	ratio of the specific heats, $c_p/c_v$
$m$	molecular weight; weight of 1 mole
$n$	a constant; the polytropic exponent
$p$	pressure, psi
$p_r$	relative pressure
$P$	pressure, psf; pressure in general
$P_R$	reduced pressure
$Q$	heat flow
$R$	gas constant
$s$	specific entropy
$S$	entropy of a system
$t$	scalar temperature
$T$	absolute temperature
$T_R$	reduced temperature
$u$	specific internal energy
$v$	specific volume
$v_r$	relative volume
$V$	volume of a system
$V_R$	reduced volume
$W$	work
$x$	mole fraction of a gas in a mixture of gases
$Z$	compressibility factor
$Z_c$	compressibility factor at the critical point

*Greek Letters*

$\alpha$	a function of the temperature
$\phi$	$\int_0^T \frac{c_p dT}{T}$ , a property of the perfect gas

*Subscripts*

$c$	at the critical point
$m$	of the mixture
$p$	constant pressure
$s$	constant entropy
$T$	constant temperature
$v$	constant volume

## CHAPTER 19

### THERMODYNAMICS OF COMBUSTION

**19:1. Introduction.** All of the power cycles that have been discussed in earlier chapters presume that a reservoir is available from which heat may be continuously withdrawn at a temperature above that of the atmosphere. If this reservoir is finite in extent and is not at the same time receiving energy at a rate at least equal to that at which it supplies heat to the working fluid of the heat engine, its temperature must ultimately decline to that of the atmosphere and the manufacture of power will cease.

The engineer provides for the continuous replenishment of the energy of the source by means of the combustion of some sort of fuel. Fuels may be solids (as coal), liquids (oil or gasoline), or may be in the form of a gas (for example, natural gas), but all have the common characteristic of containing at least some proportion of certain elements in a form such that, if they are mixed with air and ignited by means of a spark or flame, they will unite with the oxygen of the air to form new substances, at the same time releasing energy of which the engineer can make use. The process by means of which this energy is released is called *combustion*. The combination of the fuel with the air which is to supply the oxygen for combustion is given the name of the *mixture*, or the *reactants*, and the substance, or combination of substances, that results from the combustion process is termed the *products*.

The combustible elements of a fuel that are of importance to the engineer include carbon (C), hydrogen (H), and, of much less importance, sulfur (S). The combustion of carbon may produce carbon monoxide (CO) or carbon dioxide (CO<sub>2</sub>), according to the conditions that exist in the course of the reaction. If carbon monoxide is formed, the amount of energy released will be less than if the products consist of carbon dioxide but the CO is capable of a further reaction with additional amounts of oxygen that will produce CO<sub>2</sub> as the end product. Further increments of energy equal in amount (if the initial and final temperatures and pressures are the same in both cases) to the original deficit will be released; this is a requirement of the First Law. Hydrogen burns to form water (H<sub>2</sub>O) and sulfur forms SO<sub>2</sub> as a result of the engineering combustion process.

The reason for the energy release that accompanies combustion is found in the fact that a given mass of the products stores a much smaller amount



of energy than an equal mass of the reactants at the same pressure and temperature. When combustion occurs, this excess of energy may have a number of effects. If the space in which combustion takes place is surrounded by rigid walls and is insulated against heat flow, its passage as heat or work to the surroundings is prevented and it must remain as stored energy in the products. But this means that the products, in order to store the same amount of energy as the reactants originally possessed, must rise in temperature above the temperature of the mixture as the reaction began; at this elevated temperature the products provide a source from which heat may be withdrawn at high temperature for the purposes of the power cycle. If enough heat leaves the products, their temperature may be returned to the original temperature of the reactants; this heat flow then measures the amount of energy release and is called the *heat of combustion* at the temperature at which the reaction began and ended. Because the relative energy-storage capacities of the reactants and the products may differ at different temperatures, a corresponding variation of the heat of combustion according to the base temperature that is selected is to be expected.

Based upon our study of the Carnot cycle, we observe that not all of the heat of combustion may be changed to the form of work. The proportion that is available for that purpose will depend upon the temperature at which the heat of combustion can be delivered for the purposes of the cycle. As the result of combustion, the temperature of the products rises to a certain maximum which will depend upon the heat of combustion, the mass of the products, and their specific heat. The first increment of heat may be withdrawn to supply the power cycle at this maximum temperature and may be used with maximum effectiveness in the manufacture of work, although even this increment is not, as we have seen, possible of complete cyclic conversion into the more valuable form of energy. As additional amounts of heat are withdrawn, the temperature of the products declines and the effective source temperature with it, with a corresponding decrease in the efficiency of conversion into work. Assuming that combustion began at the temperature of the atmosphere, the last increments of the heat of combustion are almost entirely ineffective for the purpose of work delivery by the power cycle, for they can be delivered at temperatures only insignificantly above the temperature of the atmosphere.

A larger proportion of the energy released as the result of combustion can be converted into work if the power cycle is supplied with heat at an essentially constant temperature which is as high as is possible and practical. This implies that the combustion process shall be continuous, with a steady stream of fuel uniting with a stream of air to produce a stream of products. Heat is removed from these products for the purposes of the

power cycle, but their final temperature remains at a level such that the heat engine is not handicapped in attaining a reasonable efficiency in converting this heat into work. Since the products are not returned to the original temperature of the reactants, a part of the heat of combustion remains in those products as stored energy after they have contributed their dividend of heat to the power cycle.

The temperature at which heat can be delivered for the purposes of the power cycle is, as we have seen, important in limiting the efficiency of the heat engine; that temperature cannot exceed the maximum temperature that can result from combustion and thus, as stated above, depends not only upon the heat of combustion but also upon the mass and the specific heat of the products. The engineer obtains the oxygen for combustion from air, a gas which is a mixture of about one-fifth oxygen with four-fifths nitrogen and other inert gases. These inert gases form a part of the products as well as of the reactants and increase the mass of those products; this increased mass lowers the maximum temperature attainable. Air in excess of the minimum amount necessary to supply the oxygen required for combustion is often used by the engineer in order to ensure that each particle of fuel will have in its immediate vicinity enough oxygen to supply its needs for complete combustion; the use of excess air still further increases the weight of products per unit mass of fuel burned and limits the maximum temperature.

The heat of reaction is based on the assumption that combustion is complete. The maximum temperature that can be reached as the result of combustion is limited not alone by the possibility that the mixture of reactants is not homogeneous and that some particles of fuel may be starved for oxygen and remain unburned while other particles have an oversupply. In addition, as we shall see later, the reaction is, in limited degree, reversible. Thus if carbon dioxide, for example, is raised to high temperature, certain proportions will break down into the elements of carbon and oxygen. When the reaction takes place in this direction, it is called *dissociation*; according to the First Law, the heat of reaction must be negative in dissociation. Depending upon the temperature and pressure, there are certain fixed proportions of the compound and its elements present in a mixture that is in completely stable equilibrium, and this factor also limits the maximum temperature of the products to a level below that based on the assumption of complete combustion.

The combustion of the engineer is a controlled combustion and takes place within a confined space called the combustion space. The products of combustion come in contact with the walls which bound this space. The materials of which these walls are built are limited in the temperatures which they can withstand over long periods of time, and this often



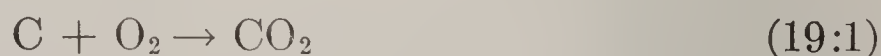
places a practical limit on the temperature at which the products may be allowed to supply heat to the working fluid of the heat engine.

The residual energy remaining in the products after they have made their direct contribution of heat for the purposes of the heat engine may be partly used. If the temperature of the reactants, instead of being the temperature of the atmosphere, had been elevated above that temperature, the maximum temperature that would have resulted from combustion would have been correspondingly, though not equally, increased. A larger fraction of the heat of combustion is therefore deliverable to the heat engine. By means of suitable heat exchangers (called air preheaters) the air for combustion can receive heat from the products after the latter have completed their commitments in the supply of heat to the power cycle and can be raised in temperature as the temperature of the products falls. Or it is often the case that all of the heat supplied the power cycle need not be furnished at the same high level of temperature. An example is found in the Rankine cycle, in which a part of the heat supplied is used to heat the liquid from the temperature of the refrigerator to the temperature at which it is evaporated. At least a part of this heat may be supplied to the liquid as it passes through a heat exchanger, called an economizer, in which it receives heat from the products after they have made their major contribution of heat to the cycle but before they are discarded to the atmosphere. In theory, the temperature of the products could, by methods such as these, be returned to approximately the temperature of the reactants, and practically all of the heat of combustion could be utilized. In practice this is not feasible, for it would require large and expensive heat exchangers and would discharge the products in a state such that some of the water vapor which they usually contain would condense and cause corrosion. Corrosion would be especially likely if the fuel contained sulfur and the products sulfur dioxide, since the combination of liquid water and sulfur dioxide would produce highly corrosive sulfurous acid. The minimum practical temperature of the products as they are finally discharged to the atmosphere is therefore about 300°F, although temperatures above that level are much more common.

Much has been said in preceding chapters about the cycle of the working fluid. In the Rankine cycle, for example, this cycle is carried out in the boiler, the prime mover, the condenser, and the liquid pump. But the real vapor power plant must also include a furnace to supply the heat that is added to the working fluid as it passes through the boiler. The substances that pass continuously through this furnace constitute a second system, which does not follow a cyclic pattern since the products of combustion are never, at least under the guidance and control of the engineer, restored to the form of the reactants that entered the process. In the

internal-combustion power plant the reactants, and later the products, constitute the working fluid and a cycle of the working fluid is not traversed. In order to study the operation of the internal-combustion engine from the standpoint of a closed cycle, it was necessary in Chap. 11 to introduce the concept of the air-standard cycle. A more realistic approach to the problem consists in analyzing the individual processes through which the fluid progresses from the time it enters the plant in the form of the reactants until it leaves as the products of a combustion that has taken place in the interim. Differences in chemical composition and in the mass that is included within the boundaries of the system under study must be considered in making this type of analysis. Some of these processes, as when the reactants enter or the products leave, are flow processes and may be analyzed as such, although truly steady-flow conditions are not always present. Others are typically nonflow in character, and the equations of Chap. 2 will apply, but with the reservation that the system is not a simple system. In either case,  $E$  replaces  $U$  and must be calculated with respect to the chemical composition of the fluid at the end points of each process.

**19:2. The Combustion Equation.** The combustible elements of importance to the engineer are carbon, hydrogen, and sulfur. To support combustion, he must also arrange for a supply of oxygen. The combustion equation provides a key to the relative quantities of the combustible and the oxygen that enter the reaction and the products that result from it. Thus, in the complete combustion of carbon to form carbon dioxide, we may write

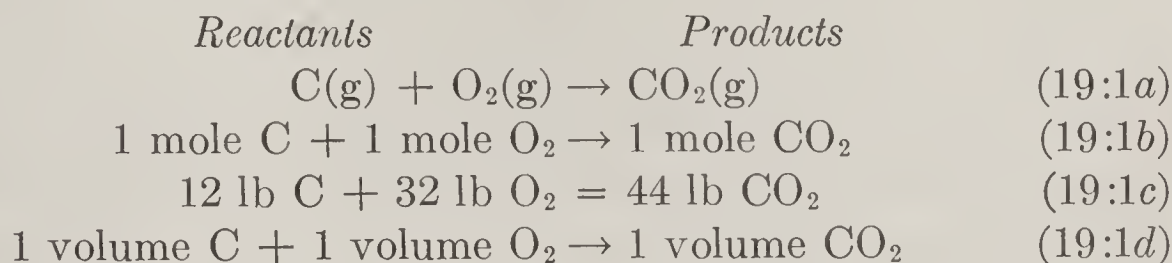


This equation may be interpreted in a number of ways. For example, it may be read as "1 molecule of carbon unites with 1 molecule of oxygen to form 1 molecule of carbon dioxide." We have already learned (Chap. 9) that a mole is a standard number of molecules, and the magnitude of the reaction as originally described can be multiplied by this number; the equation can correspondingly be read as describing the union of 1 mole of carbon with 1 mole of oxygen to form 1 mole of carbon dioxide. It will be observed that it is not necessary that the number of moles of the products shall equal the number of moles of the reactants. On the other hand, it is required that a mass balance shall exist on the two sides of the equation. The weight of the standard number of molecules that is described as 1 lb-mole is numerically equal, in pounds, to the molecular weight  $m$ . Thus Eq. (19:1) may be interpreted as describing the reactants as consisting of 12 lb of carbon, 32 lb of oxygen, while the weight of  $\text{CO}_2$  that constitutes the products is 44 lb. If all of the substances that enter into the reaction and result from it are gases and their pressure is low enough

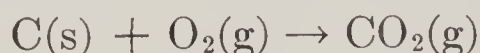


so that they can be considered to be perfect gases, their volumes, at the same pressure and temperature, will be in proportion to the relative number of moles of each that takes part in the reaction. Thus, if the carbon reactant in Eq. (19:1) is a gas, we may interpret the equation as representing the union of 1 volume of carbon with 1 volume of oxygen to form 1 volume of carbon dioxide; the inference is, of course, that these volumes are being measured at the same pressure and temperature, *i.e.*, that the products are at the same pressure and temperature as the reactants. On the other hand, it is quite possible that the carbon may be in the solid or the liquid phase as it enters the reaction, in which case its volume would be negligible as compared with the molal volume of the gaseous oxygen and carbon dioxide; if this qualification were made, we should be forced to alter our statement to indicate that the volume of products equals the volume of the reactants for this particular reaction. Thus, if the combustion equation is to be read in terms of the relative volumes of the reactants and the products, the phase of the fuel as it enters the combustion must be specified. This specification is often made by using the parentheses-enclosed letters (s), (l), or (g), meaning, respectively, solid, liquid, and gas, after each of the reactants and the products to indicate their phase and to guide the reader in estimating relative volumes.

Let us review the various interpretations of Eq. (19:1).



Of these equations [note, however, that only (19:1c) is, of necessity, an equality] 19:1d is an approximation which is based on the assumption that the reactants and the products are perfect gases and that the volume of reactants and products is measured at the same pressure and temperature. If (19:1a) had been written

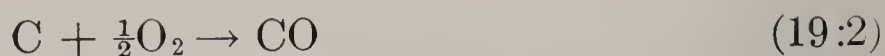


(19:1d) would have undergone a change to the form



and the volume of reactants and products would have been the same. An additional approximation has thus been introduced in considering the volume of the solid to be negligible.

In addition to Eq. (19:1), the basic combustion equations with which the engineer is concerned are



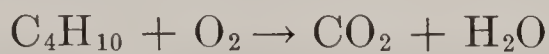
For each of these basic reactions, a set of expressions analogous to (19:1*a*) to (19:1*d*) may be framed from which the relative number of moles, the weights, and the volumes of reactants and products may be obtained and compared when pure oxygen is supplied for the purposes of combustion. But the engineer furnishes oxygen in the dilute form of air, which is essentially a mixture of 0.21 mole of oxygen per 0.79 mole of inert nitrogen, and the mass and volume of both reactants and products are correspondingly increased. Per mole of oxygen entering the reaction,  $\frac{7.9}{2.1}$ , or 3.76, moles of nitrogen are also introduced and will appear in the products, since this nitrogen takes no active part in the chemical change. Thus when exactly enough air is furnished to supply the oxygen necessary to burn the carbon to  $\text{CO}_2$ , Eq. (19:1) becomes



and calculation indicates that the proportion of the moles of products to the moles of reactants is 4.76:5.76 while the weight balance is as follows:



The fuels with which the engineer deals are almost invariably more complicated combinations of combustible elements than are contemplated in the basic combustion equations (19:1) to (19:5). They may also, as in coal, contain considerable percentages of noncombustible substances. Let us see how the basic equations may be applied in writing the combustion equation for butane ( $\text{C}_4\text{H}_{10}$ ), for example. It will be assumed that combustion is complete (C to  $\text{CO}_2$ ); the products will therefore consist of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and we may write the combustion equation in unbalanced form (showing each of the reactants and each of the products but not the number of molecules of each) as



Noting that the same number of carbon atoms must appear in both reactants and products, we see that the number of molecules of  $\text{CO}_2$  must be 4. In a similar manner, based on a balance of the number of atoms of hydrogen, the number of molecules of  $\text{H}_2\text{O}$  that will appear in the products is evidently 5. The number of atoms of oxygen in 4 molecules of  $\text{CO}_2$  is 8, and the number of oxygen atoms in 5 molecules of  $\text{H}_2\text{O}$  is 5, a total of 13 atoms of oxygen; to balance the equation requires that  $6\frac{1}{2}$  molecules be



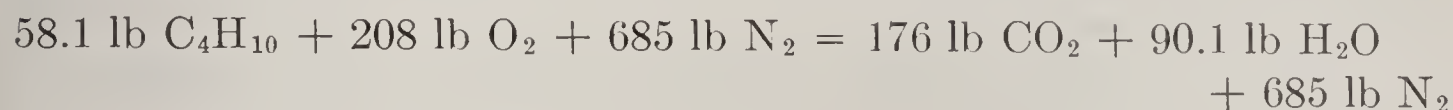
included in the reactants. The balanced equation may then be written as



The equation may now be read in terms of moles rather than molecules. If the oxygen is furnished in air, it will be necessary to add  $(6\frac{1}{2})(3.76) = 24.44$  moles of nitrogen to both reactants and products in Eq. (19:7), or



The weight balance for this equation may now be written as



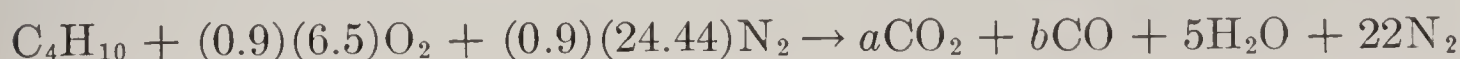
The *air-fuel ratio* is often a matter of interest to the engineer; this is the ratio of the mass of air supplied for combustion to the mass of fuel. For the combustion that is represented by Eq. (19:8), the mass of air supplied to burn 1 mole, or 58.1 lb, of fuel is the sum of the masses of the oxygen and the nitrogen in the reactants, or 893 lb; the air-fuel ratio is therefore  $893/58.1 = 15.4$  lb air per pound  $\text{C}_4\text{H}_{10}$ .

The value of 15.4 lb of air per pound of  $\text{C}_4\text{H}_{10}$  which is derived as the air-fuel ratio above is based on supplying the minimum amount of air that could furnish the oxygen necessary for complete combustion; this is called the *theoretical air*.

The engineer cannot obtain a mixture of fuel and air such that sufficient oxygen will be available to each particle of fuel for its complete combustion without providing what he calls *excess air*, *i.e.*, air in excess of the theoretical requirements. He expresses the amount of this excess air as a percentage based upon the theoretical. Thus if 10 per cent excess air is supplied in the combustion of  $\text{C}_4\text{H}_{10}$ , the weight of air supplied must be  $(1.1)(893) = 982$  lb per 58.1 lb of  $\text{C}_4\text{H}_{10}$ , corresponding to an air-fuel ratio of  $982/58.1 = 16.9$  lb of air per pound of  $\text{C}_4\text{H}_{10}$ . The extra oxygen and nitrogen will appear in unchanged form in the products. Based upon 10 per cent excess air, Eq. (19:8) would assume the form



On the other hand, insufficient air may be provided for complete combustion. If the deficit is small, it will, in the combustion of a hydrocarbon, probably result in the presence of a proportion of CO in the products; if large, free carbon, or even free hydrogen, may appear. As an example, let us assume that 90 per cent of the theoretical air is supplied in burning  $\text{C}_4\text{H}_{10}$  and that the products consist only of  $\text{CO}_2$ , CO,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ . We may then write the equation in the form



in which  $a$  and  $b$  are, respectively, the number of molecules of  $\text{CO}_2$  and  $\text{CO}$  in the products per molecule of  $\text{C}_4\text{H}_{10}$  in the reactants. Based on the necessary balance of carbon atoms,

$$a + b = 4$$

A similar balance of the number of oxygen atoms requires that

$$2a + b + 5 = (2)(0.9)(6.5) = 11.7$$

Solving these two equations simultaneously,  $a = 2.7$  and  $b = 1.3$ . The balanced equation is

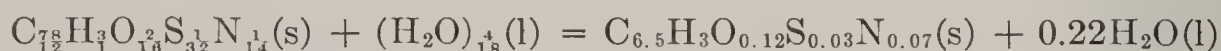


*Example 19:2.* The fuel is coal with an ultimate analysis<sup>1</sup> as follows,

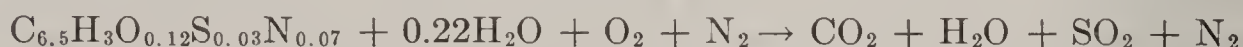
C, 78; H, 3; O, 2; S, 1; N, 1;  $\text{H}_2\text{O}$ , 4; ash, 11

in which C, H, O, S, and N are the corresponding elements,  $\text{H}_2\text{O}$  is the surface moisture, and the ash is a mixture of noncombustible substances. The figures give the percentages by mass of each constituent. Write the combustion equation for 100 lb of this coal, and calculate the air-fuel ratio ( $a$ ) when complete combustion is assumed with theoretical air supplied, ( $b$ ) when complete combustion is assumed with 50 per cent excess air, and ( $c$ ) when the air supplied is 90 per cent of the theoretical but the hydrogen and sulfur burn completely and there is no free oxygen in the products.

*Solution.* The weight of 100 lb is an artificial mole unit often used by the engineer in analyzing the combustion of fuels which, like coal, are described in terms of their ultimate analyses. Thus 1 "mole" of this coal contains 78 lb of carbon, 3 lb of hydrogen (in addition to the hydrogen in the surface moisture), etc. Dividing these weights by the atomic weights, an equivalent chemical formula for the coal (exclusive of the ash, which is noncombustible and does not take part in, or change its phase as the result of, the reaction) is



(a) Writing the unbalanced equation,



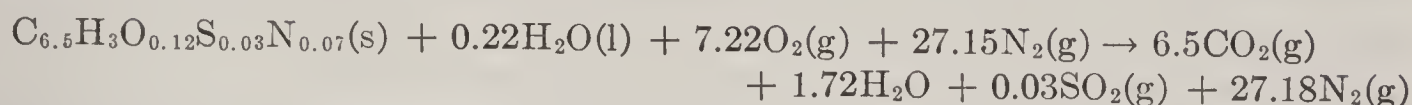
The number of hydrogen atoms in the reactants is  $3 + (2)(0.22) = 3.44$ . The number of moles of  $\text{H}_2\text{O}$  in the products must therefore be  $3.44/2 = 1.72$ . The number of moles of  $\text{CO}_2$  in the products must be equal to the number of carbon atoms in the reactants, or 6.5. Similarly, based on a balance of a sulfur atoms, the number of moles of  $\text{SO}_2$  in the products is 0.03.

Placing these coefficients on the right side of the equation, the number of atoms of oxygen in the products is calculated as  $(6.5)(2) + 1.72 + (0.03)(2) = 14.78$ . Subtracting the number of atoms of oxygen in the fuel, the number of moles of  $\text{O}_2$  in the reactants is calculated as  $(14.78 - 0.12 - 0.22)/2 = 7.22$ . The number of moles of

<sup>1</sup> The ultimate analysis states the percentages of the masses of the various constituents, *i.e.*, is expressed on a gravimetric basis. It is usually employed in describing solid or liquid fuels. A volumetric analysis is often used when the fuel is a gas and may be converted to the gravimetric basis by applying the methods of Chap. 10.

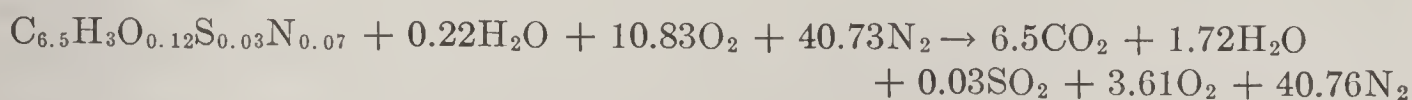


nitrogen in both reactants and products is  $0.07/2 + (3.76)(7.22) = 27.18$ . The balanced equation may now be written as



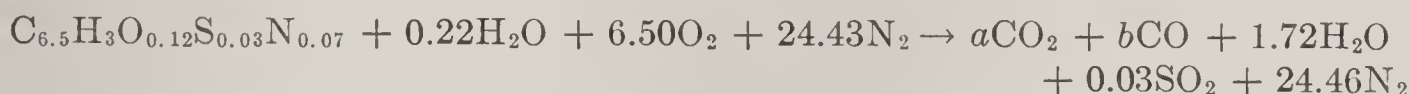
The air-fuel ratio is  $\frac{(7.22)(32) + (27.15)(28)}{100} = 9.91$  lb air per pound coal.

(b) The use of 50 per cent excess air will increase the number of moles of  $\text{O}_2$  in the reactants by  $(0.5)(7.22) = 3.61$ , making a total of 10.83 moles. The extra 3.61 moles will appear as  $\text{O}_2$  in the products. The number of moles of  $\text{N}_2$  in both reactants and products will be increased in the same proportion, or by 13.58 moles. The combustion equation is



The air-fuel ratio is  $(1.5)(9.91) = 14.87$  lb of air per pound of coal.

(c) The number of moles of  $\text{O}_2$  in the reactants is  $(0.9)(7.22) = 6.50$ . The number of moles of  $\text{N}_2$  is, similarly, 24.43. Writing the combustion equation in partially balanced form,



where  $a$  and  $b$  are, respectively, the unknown number of moles of  $\text{CO}_2$  and  $\text{CO}$  that are formed as the result of the combustion of 100 lb of coal. A balance based on the number of carbon atoms shows that

$$a + b = 6.5$$

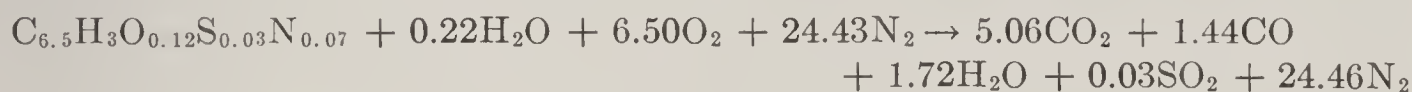
Balancing the number of oxygen atoms, we may write

$$0.12 + 0.22 + (6.5)(2) = 2a + b + 1.72 + (0.03)(2)$$

or

$$2a + b = 11.56$$

Solving simultaneously,  $a = 5.06$  and  $b = 1.44$ . The combustion equation becomes



The air-fuel ratio is  $(0.9)(9.91) = 8.92$  lb of air per pound of coal.

**19:3. Analysis of Products.** In setting up the combustion equations of the preceding article, it has been necessary to make certain assumptions. Chiefly, these assumptions have concerned the substances of which the products are composed. For example, in analyzing the combustion of  $\text{C}_4\text{H}_{10}$  with insufficient air for complete combustion, it has been assumed that all of the oxygen entered into some sort of combustion with the combustible elements of the fuel. Yet it is entirely possible that, owing to incomplete mixing of fuel and air, this would not be the case and some free oxygen would be present in the products. Similarly, even when excess air is provided, the products may include carbon monoxide. The

reaction equation can be accurately written only with a knowledge of the composition of the products, and without this information the engineer is handicapped in taking steps toward the improvement of combustion conditions in order to obtain the maximum from his fuel.

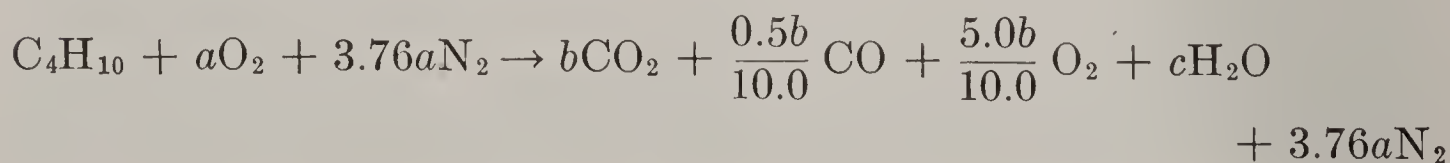
An incomplete analysis of the products is usually satisfactory for the engineer's purposes if he has a fairly accurate knowledge of the composition of the fuel. This analysis of the products of combustion (usually called a *flue-gas analysis*) is customarily made on a volumetric basis, using the Orsat apparatus. The method consists in withdrawing some of the gas and segregating a sample of standard volume, as measured at atmospheric pressure and temperature, in a burette designed for that purpose. This sample is then passed through a solution of potassium hydroxide that will absorb  $\text{CO}_2$  and returned to the measuring burette, where, again at atmospheric temperature and pressure, the remaining volume is noted; the volumetric percentage of  $\text{CO}_2$  is determined by difference. The free oxygen is next removed by passing what remains of the original sample through a solution of pyrogalllic acid; the remaining volume is again measured to obtain, by difference, the volumetric percentage of oxygen. Finally, a solution of cuprous chloride removes the CO from the part of the sample still remaining and makes possible the determination of the volumetric percentage of that constituent. The remaining volume is assumed to represent the percentage of nitrogen. The sample also contains water vapor which is not removed, but the partial pressure of the water vapor remains constant since the conditions under which the volume is measured are such as to ensure that it will be saturated with water vapor and since the temperature remains constant throughout the analysis. Thus the volumetric proportions of  $\text{CO}_2$ ,  $\text{O}_2$ , CO, and "nitrogen" are obtained on the dry basis, *i.e.*, as if the water vapor had been removed from the sample prior to its analysis. Additional solutions for the removal of other gases may be added if a more detailed analysis is desired; sometimes an analysis for  $\text{CO}_2$  alone is made.

As an example of a way in which the engineer may make use of an analysis of the products of combustion, let it be supposed that in the burning of butane the following Orsat analysis (volumetric, dry basis) is obtained:

$\text{CO}_2$ , 10.0%;  $\text{O}_2$ , 5.0%; CO, 0.5%;  $\text{N}_2$  (by difference), 84.5%

The air-fuel ratio and the per cent of excess air are required.

The combustion equation may be written as





in which  $a$  is the number of moles of oxygen supplied,  $b$  is the number of moles of  $\text{CO}_2$ , and  $c$  is the number of moles of  $\text{H}_2\text{O}$  in the products per mole of  $\text{C}_4\text{H}_{10}$  burned. The number of moles of nitrogen, it will be noted, bears a fixed ratio to the number of moles of oxygen which is based on their relative proportions in air; the number of moles of nitrogen in reactants and products must be the same. The number of moles of  $\text{CO}$  and of  $\text{O}_2$  in the products similarly bear fixed ratios to the number of moles of  $\text{CO}_2$ , ratios which are based on the relative percentages as shown by the Orsat analysis.

From a hydrogen balance,

$$c = 5$$

From a carbon balance,

$$b + \frac{0.5b}{10.0} = 4 \quad \text{or} \quad b = 3.81$$

From an oxygen balance,

$$2a = 2b + \frac{0.5b}{10.0} + \frac{5.0}{10.0} \quad 2b + 5 \quad \text{or} \quad a = 8.31$$

Substituting these values in the combustion equation,

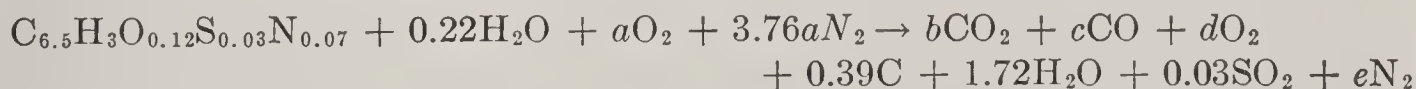


The weight of air supplied per mole of  $\text{C}_4\text{H}_{10}$  is  $(8.31)(32) + (31.2)(28) = 1140$  lb. The air-fuel ratio  $= 1140/58.1 = 19.6$  lb per pound  $\text{C}_4\text{H}_{10}$ . This corresponds to  $19.6/15.4 - 1 = 0.27$ , or 27 per cent excess air.

The data may now be checked for a reasonable degree of consistency. It will be noted that the number of moles of nitrogen in the products might also have been expressed in a proportion based on the Orsat analysis as  $84.5b/10.0 = (8.45)(3.81) = 32.2$  moles. This checks the number as based on the oxygen supplied within approximately 3 per cent, about as close agreement as can be expected.

*Example 19:3.* In burning the coal of Example 19:2, an Orsat analysis shows the following percentages by volume for the gaseous products:  $\text{CO}_2$ , 12 per cent;  $\text{O}_2$ , 7 per cent;  $\text{CO}$ , 0.5 per cent;  $\text{N}_2$  (by difference), 80.5 per cent. An analysis of the cinder in the ash pit shows it to be 30 per cent unburned carbon. Write the combustion equation, and determine the percentage of excess air.

*Solution.* The weight of ash is 11 lb per "mole" of coal. If the cinder is 30 per cent unburned carbon, the total weight of cinder is  $11/0.7 = 15.7$  lb per 100 lb of coal, and 4.7 lb (4.7/12 mole) of carbon remains unburned. A partially balanced combustion equation may be written.



Based on a balance of carbon atoms,

$$b + c = 6.5 - 0.39 = 6.11 \tag{1}$$

From an oxygen balance,

$$0.12 + 0.22 + 2a = 2b + c + 2d + 1.72 + 0.06$$

or

$$2a - 2b - c - 2d = 1.44 \quad (2)$$

From the Orsat analysis,

$$c = \frac{0.5}{12} b = 0.0417b \quad (3)$$

and

$$d = \frac{7}{12} b = 0.583b \quad (4)$$

From Eqs. (1), (3), and (4),

$$b = 5.87; c = 0.24; d = 3.42$$

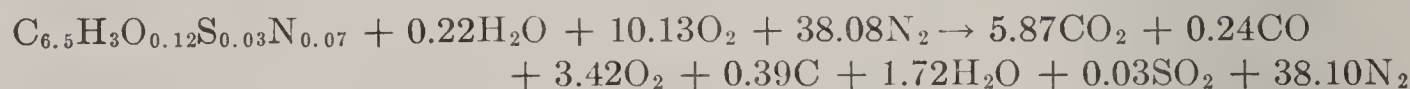
Substituting these values in (2),

$$a = 10.13$$

Making a nitrogen balance,

$$e = \frac{0.07 + (3.76)(10.13)(2)}{2} = 38.10$$

The combustion equation may now be written:



From the solution to Example 19:2(a), the number of moles of oxygen in the theoretical air is 7.22. In the present example, therefore

$$\text{Excess air} = \frac{10.13 - 7.22}{7.22} = 0.403, \text{ or } 40.3 \text{ per cent}$$

Checking the combustion equation, it is noted that the number of moles in the products is 38.10. From the Orsat analysis, the ratio  $e/b$  should be in the proportion  $80.5/12 = 6.7$ ; or  $e = 6.7b = (6.7)(5.87) = 39.4$ . This would be considered in fairly close agreement.

**19:4. The heat of combustion** is a measure of the heat that may be liberated as a result of the combustion reaction if the products are returned to the original temperature of the reactants. This heat flow, when positive, is away from the system which undergoes the reaction; the convention as to sign in chemistry is thus opposite to that which we have used in thermodynamics, and this must be kept in mind as the basic thermodynamic relations are applied.

The heat of combustion of solids and liquids is usually measured experimentally by means of a bomb calorimeter. This is a rigid-walled vessel in which a carefully measured sample of the fuel is placed, together with oxygen in an amount more than sufficient to ensure complete combustion.



The vessel, after being closed, is placed in a water bath, and the fuel is ignited by means of an electric current. As the fuel burns, the temperature of the bomb and the water will rise only moderately because of the high capacity for energy storage of the water bath; although the final temperature is somewhat above the initial temperature of the reactants, allowance may be made for this and other factors in calculating the heat of combustion.

In the bomb-calorimeter process, the system is a closed system, and the combustion takes place at constant volume; the heat of combustion as determined by this method is called the *constant-volume heat of combustion*. No work accompanies the reaction. Taking into consideration the reversal of the sign convention to which attention has been directed above, Eq. (2:2) may be applied to write

$$Q_v = -_1Q_2 = [E_1 - E_2]_T = [E_{\text{mixture}} - E_{\text{products}}]_T \quad (19:9)$$

in which  $Q_v$  is the constant-volume heat of combustion, the subscripts 1 and 2 refer, respectively, to the beginning and to the end of the combustion process, and  $E$  (for total stored energy) is used since this is not a simple system. The subscript  $T$  indicates that the values of  $E$  must be based on the same (base) temperature. We may substitute  $U_{\text{mixture}}$  and  $U_{\text{products}}$ , respectively, for  $E_{\text{mixture}}$  and  $E_{\text{products}}$  in Eq. (19:9) if  $U$  for the products not only is measured at the same temperature at which the internal energy of the mixture is measured but also is based on the same reference level of total stored energy.<sup>1</sup> On this basis the heat of combustion at constant volume, obtained experimentally, measures the difference between the internal energy of the mixture and the internal energy of the products at the same temperature, and we may write

$$Q_v = [U_{\text{mixture}} - U_{\text{products}}]_T = [-\Delta U]_T \quad (19:10)$$

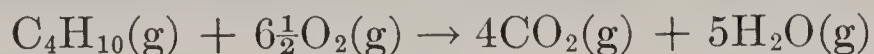
The fuel tested in the bomb calorimeter is characteristically a solid or a liquid and thus occupies negligible volume. Also, when  $\text{H}_2\text{O}$  is among the products, almost all will appear as a liquid instead of a gas in those products because of the low final temperature and the limited volume of the calorimeter. Thus the combustion equation for butane, for example, as that combustion is carried out in the bomb calorimeter, would appear as



The value of the heat of combustion that is obtained in the use of the bomb calorimeter is based on these specifications as to the phase of the various substances that enter into and result from the reaction. However, if it is desired to obtain the constant-volume heat of combustion

<sup>1</sup> Thus  $U$  would include chemical energy.

that corresponds to the combustion equation



all that is necessary is to add to the bomb-calorimeter value the internal energy of vaporization of  $\text{C}_4\text{H}_{10}$  and subtract the internal energy of vaporization of  $\text{H}_2\text{O}$ , both at the base temperature to which the reaction is referred.

Returning to Eq. (19:10), the rate of change of internal energy with temperature will usually differ somewhat for the products from the similar rate of change for the mixture, indicating that the difference  $-\Delta U$  of that equation will depend upon the base temperature at which the reaction is begun and concluded. Thus the heat of combustion must be stated with reference to this base temperature; the standard base temperature is  $25^\circ\text{C}$ , equivalent to  $77^\circ\text{F}$ . A change to any other base temperature may be made if the specific heats of the mixture and of the products are known, so that the changes of internal energy of mixture and of products over the temperature interval may be calculated and compared.

The heat of combustion of gases is usually obtained experimentally by the use of the steady-flow gas calorimeter. In this device the steadily flowing stream of fuel is mixed with a stream of air that carries more than sufficient oxygen to ensure complete combustion and is burned continuously. The fuel supply is measured volumetrically by means of a gas meter. The products are cooled to the initial temperature of the reactants by means of a water jacket. The rise in temperature of the water passing through this jacket is a key to the *constant-pressure heat of combustion*, since the reaction takes place at constant pressure.

The gas calorimeter is a steady-flow device and the system is an open system; Eq. (3:5) may be applied, giving

$$Q_p = -{}_1Q_2 = [H_{\text{mixture}} - H_{\text{products}}]_{T,p} = [-\Delta H]_{T,p} \quad (19:11)$$

in which  $Q_p$  is the constant-pressure heat of combustion and the subscripts 1 and 2 again refer to states at the beginning and at the end of the reaction.  $H_{\text{mixture}}$  and  $H_{\text{products}}$  are measured at the same pressure and temperature, as is indicated by the subscripts  $T$  and  $p$ , and are based on the same total weight and the same reference state ( $U$  includes chemical stored energy). The phase in which each of the substances that compose the mixture and the products appears will affect the constant-pressure heat of combustion as it did the heat of combustion at constant volume, but again an allowance may be made for a difference in this respect, this time by means of an adjustment based on the enthalpy of vaporization instead of the internal energy of vaporization, as when adjusting the constant-volume heat of combustion to differences in phase.



TABLE 19:1. CONSTANT-PRESSURE HEATS OF COMBUSTION\*  
At 77°F

Basic combustion equations						
Fuel	Formula	Phase of fuel	Combustion equation		$-\Delta H$ , Btu/ lb fuel	
Hydrogen.....	H <sub>2</sub>	Gas	H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O(1)		60,958	
Carbon.....	C	Solid	C(s) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)		14,087	
Carbon monoxide	CO	Gas	CO(g) + $\frac{1}{2}$ O <sub>2</sub> (g) → CO <sub>2</sub> (g)		4,344	
Sulfur.....	S	Solid	S(s) + O <sub>2</sub> (g) → SO <sub>2</sub> (g)		3,940	

Hydrocarbons						
Fuel	Formula	Phase of fuel	Phase of products		$-\Delta H$ , Btu/ lb fuel	$h_{fg}$ of fuel at 77°F, Btu/ lb fuel
			CO <sub>2</sub>	H <sub>2</sub> O		
Methane.....	CH <sub>4</sub>	Gas	Gas	Liquid	23,861	
Ethane.....	C <sub>2</sub> H <sub>6</sub>	Gas	Gas	Liquid	22,304	
Butane.....	C <sub>4</sub> H <sub>10</sub>	Gas	Gas	Liquid	21,293	159
Pentane.....	C <sub>5</sub> H <sub>12</sub>	Gas	Gas	Liquid	21,072	158
Heptane.....	C <sub>7</sub> H <sub>16</sub>	Gas	Gas	Liquid	20,825	157
Octane.....	C <sub>8</sub> H <sub>18</sub>	Gas	Gas	Liquid	20,747	156
Benzene.....	C <sub>6</sub> H <sub>6</sub>	Gas	Gas	Liquid	18,172	186
Decane.....	C <sub>10</sub> H <sub>22</sub>	Gas	Gas	Liquid	20,638	154
Dodecane.....	C <sub>12</sub> H <sub>26</sub>	Gas	Gas	Liquid	20,564	154
Hexadecane.....	C <sub>16</sub> H <sub>34</sub>	Gas	Gas	Liquid	20,472	154

\* Chiefly from API Research Project 44, National Bureau of Standards.

In Table 19:1 are shown data regarding the constant-pressure heat of combustion ( $-\Delta H$ ) of various fuels. The heat of combustion is here measured at a base temperature of 77°F and is based on phases of fuel and of products as indicated in the table. Methods have already been discussed by means of which the tabulated heats of combustion may be adjusted to different phases of the fuel or of the products. For example, let it be required to calculate  $-\Delta H$  when butane enters the reaction as a liquid and the H<sub>2</sub>O in the products is a gas. From an earlier computation [see Eq. (19:7)], 5 moles, or 90 lb, of H<sub>2</sub>O are formed in the complete combustion of 1 mole, or 58 lb, of C<sub>4</sub>H<sub>10</sub>. From the steam tables, the enthalpy of vaporization of H<sub>2</sub>O at 77°F is 1050.4 Btu/lb. Since heat given up owing to condensation of H<sub>2</sub>O in the products forms a part of  $-\Delta H$  as tabulated here, we shall deduct  $\frac{90}{58}$  (1050.4) = 1630 Btu from 21,293, the value of  $-\Delta H$  from Table 19:1, giving 19,663 Btu per pound of fuel as the constant-pressure heat of combustion when the H<sub>2</sub>O of the products is a

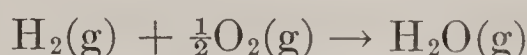
gas. If the butane had entered the reaction as a liquid, the table shows that 159 Btu of the heat generated would have been used in changing it to the gaseous phase. The net value of the constant-pressure heat of combustion under these new conditions is therefore  $19,663 - 159 = 19,504$  Btu per pound of butane.

The heat of combustion, when based on the assumption that the  $\text{H}_2\text{O}$  in the products is a liquid, is called the *higher heating value*; if a gas, the term *lower heating value* is used. With the exception of the combustion of carbon, carbon dioxide, and sulfur, where no  $\text{H}_2\text{O}$  is formed, all of the values of  $-\Delta H$  in Table 19:1 are higher heat values. There is of course no distinction to be made between higher and lower heat value when  $\text{H}_2\text{O}$  does not appear in the products.

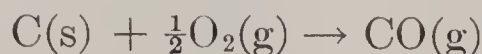
The heat of combustion at constant pressure may be larger, may be smaller, or may be equal to the heat of combustion at constant volume. We may write

$$\begin{aligned} -\Delta H &= H_{\text{mixture}} - H_{\text{products}} = E_{\text{mixture}} - E_{\text{products}} + \frac{P}{J} (V_{\text{mixture}} - V_{\text{products}}) \\ &= -\Delta E + \frac{P}{J} (V_{\text{mixture}} - V_{\text{products}}) \end{aligned} \quad (19:12)$$

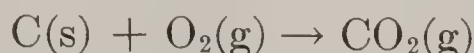
Thus it is observed that if the volume of the mixture is greater than the volume of the products, when measured at the same pressure and temperature,  $-\Delta H > -\Delta E$ . If the two volumes are equal, the two heats of combustion are equal, and if the volume of the products exceeds the volume of the mixture,  $-\Delta H < -\Delta E$ . The combustion equation furnishes the key as to the relative volumes of mixture and products, as we have seen. For example, when the combustion equation is



the volume of the mixture is greater than the volume of the products, as measured at the same pressure and temperature, and  $-\Delta H > -\Delta E$ . On the other hand, for



the opposite is true, while for

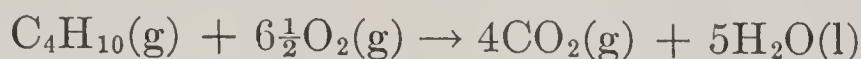


the volumes are equal, and  $-\Delta H = -\Delta E$ .

This principle may be used to obtain the constant-volume heat of combustion from the constant-pressure heat of combustion, or vice versa. In performing the calculation, it is customary to assume that the gases are



perfect gases. For example, let it be required to find the constant-volume heat of combustion that corresponds to the following combustion equation:



$-\Delta H$  is given for this reaction in Table 19:1 as 21,293 Btu per pound of  $\text{C}_4\text{H}_{10}$ . In the combustion of 1 mole, 58 lb, of the fuel, there are  $7\frac{1}{2}$  moles of the mixture, 9 moles of the products; of the products, 4 moles are in the gaseous phase. This represents a reduction of  $3\frac{1}{2}$  moles in volume as a result of the reaction. The product  $PV$  for 1 mole of a perfect gas is [see Art. 9:2 and Eq. (9:2)]

$$PV = Pmv = 1545T$$

Thus in Eq. (19:12),

$$\begin{aligned} \frac{P}{J} (V_{\text{mixture}} - V_{\text{products}}) &= \frac{(PV)_{\text{mixture}} - (PV)_{\text{products}}}{J} \\ &= \frac{(3\frac{1}{2})(1545)(460 + 77)}{778} \\ &= 3740 \text{ Btu per mole } \text{C}_4\text{H}_{10} \\ &= 64 \text{ Btu per pound of } \text{C}_4\text{H}_{10} \end{aligned}$$

Substituting this value in Eq. (19:12),

$$Q_v = -\Delta E \text{ per lb} = -\Delta H - 64 = 21,293 - 64 = 21,229 \text{ Btu/lb}$$

*Example 19:4.* For the coal of Example 19:2, calculate (a) the higher heat value in constant-pressure combustion; (b) the lower heat value in constant-pressure combustion; (c) the higher heat value in constant-volume combustion. The base temperature is 77°F.

*Solution:*

(a) The weight of carbon per "mole" of coal is 78 lb. The heat value of this carbon, based on Table 19:1, is  $(78)(14,087) = 1,098,786$  Btu per mole of coal. The hydrogen in the  $\text{H}_2\text{O}$  is, of course, not available for combustion. The rest of the hydrogen in the coal, because of its affinity for oxygen, is also assumed to be in combination with the oxygen of the fuel to the extent that the amount of oxygen permits. In the formation of  $\text{H}_2\text{O}$ , 8 lb of oxygen unites with each pound of hydrogen. Therefore, from the 3 lb of hydrogen in a mole of this coal, we must deduct  $\frac{1}{8}$  of the weight of oxygen it contains, or  $\frac{2}{8} = 0.25$  lb. (This is often expressed in formulas as  $\text{H} - \text{O}/8$ .) The higher heat value of the remaining 2.75 lb of hydrogen is  $(2.75)(60,958) = 167,635$  Btu per mole of coal. The single pound of sulfur in 1 mole of the coal will contribute 4344 Btu to the heating value of each mole. The relative insignificance of this contribution will be noted. Totaling, the higher heat value per mole of coal is

$$1,098,786 + 167,635 + 4344 = 1,270,765 \text{ Btu per 100 lb} = 12,708 \text{ Btu per pound of coal}$$

(b) In the combustion of 100 lb of coal, 1.72 moles, or 31 lb, of  $\text{H}_2\text{O}$  appears in the products (see Example 19:2). The enthalpy of vaporization of this weight of water vapor at 77°F is  $(31)(1050.4) = 32,600$  Btu per mole of coal. The lower heat value of the coal is therefore

$$1,270,765 - 32,600 = 1,238,165 \text{ Btu per 100 lb} = 12,382 \text{ Btu per pound of coal}$$

(c) Returning to Example 19:2, it will be seen that the number of gaseous moles in the reactants is  $7.22 + 27.15 = 34.37$ , while, for the products, it is  $6.5 + 0.03 + 27.18 = 33.68$ . (The  $\text{H}_2\text{O}$  in the products is not counted as a gas since the higher heat value is desired.) The small decrease of  $34.37 - 33.68 = 0.69$  mole per 100 lb of coal is caused by the presence of uncombined hydrogen in the coal. Note that this difference would be unchanged if excess air were used to ensure complete combustion, for the number of gaseous moles in reactants and products would both be increased in the same amount. Then

$$\begin{aligned} \frac{P}{J} (V_{\text{mixture}} - V_{\text{products}}) &= \frac{(PV)_{\text{mixture}} - (PV)_{\text{products}}}{J} = \frac{(0.69)(1545)(537)}{778} \\ &= 853 \text{ Btu per 100 lb} = 8.53 \text{ Btu per pound of coal.} \end{aligned}$$

From Eq. (19:12),

$$-\Delta E = -\Delta H - \frac{P}{J} (V_{\text{mixture}} - V_{\text{products}}) = 12,708 - 8 = 12,700 \text{ Btu/lb.}$$

**19:5. The heat of formation** is the enthalpy of a compound relative to that of the elements of which it is composed; it is stated with reference to a selected base temperature. It is thus equivalent to the constant-pressure heat of reaction (note that this is not necessarily a “combustion”) when the reactants consist of the elements and the products exclusively of the compound. Thus the heat of formation of  $\text{CO}_2$ , when the carbon enters the reaction as a solid, is  $(12)(14,087) = 169,044$  Btu/mole at the base temperature of  $77^\circ\text{F}$ . This is  $-\Delta H$ , and if the enthalpy of solid carbon and gaseous oxygen at this temperature are arbitrarily assigned a value of zero, the enthalpy per mole of  $\text{CO}_2$  at the same temperature is  $-169,044$  Btu. This relation may be written in the form of an equation as

$$H_{\text{C(s)}} + H_{\text{O}_2(\text{g})} = H_{\text{CO}_2(\text{g})} + 169,044$$

or

$$-169,044 = H_{\text{CO}_2(\text{g})} - H_{\text{C(s)}} - H_{\text{O}_2(\text{g})} \quad (\text{H in Btu/mole}) \quad (19:13)$$

Similarly, based on data from Table 19:1, we may write

$$-122,890 = H_{\text{H}_2\text{O(l)}} - H_{\text{H}_2(\text{g})} - \frac{1}{2}H_{\text{O}_2(\text{g})} \quad (19:14)$$

If the heat of formation of any hydrocarbon is known, Eqs. (19:13) and (19:14) may be used to calculate its constant-pressure heat of combustion. Conversely, if the constant-pressure heat of combustion of a fuel compound is known, its heat of formation may be computed. Let it be required, for example, to determine the heat of formation of butane. The reaction relation for butane which is analogous to, and is obtained in the same manner as, Eqs. (19:13) and (19:14) is

$$-1,237,000 = 4H_{\text{CO}_2(\text{g})} + 5H_{\text{H}_2\text{O(l)}} - H_{\text{C}_4\text{H}_{10}(\text{g})} - 6\frac{1}{2}H_{\text{O}_2(\text{g})} \quad (19:15)$$

Equations 19:13 to 19:15 may be arranged as below, multiplying each



term of an equation by a constant, if necessary, and/or changing signs to give

$$\begin{array}{rcl}
 +1,237,000 & = & -4H_{\text{CO}_2(\text{g})} - 5H_{\text{H}_2\text{O}(\text{l})} + H_{\text{C}_4\text{H}_{10}(\text{g})} + 6\frac{1}{2}H_{\text{O}_2(\text{g})} \\
 -676,176 & = & +4H_{\text{CO}_2(\text{g})} \qquad \qquad \qquad -4H_{\text{O}_2(\text{g})} - 4H_{\text{C}(\text{s})} \\
 -614,450 & = & \qquad \qquad \qquad + 5H_{\text{H}_2\text{O}(\text{l})} \qquad \qquad \qquad -2\frac{1}{2}H_{\text{O}_2(\text{g})} \qquad \qquad -5H_{\text{H}_2(\text{g})}
 \end{array}$$

Adding, we obtain

$$-53,626 = \qquad \qquad \qquad + H_{\text{C}_4\text{H}_{10}(\text{g})} \qquad \qquad \qquad -4H_{\text{C}(\text{s})} - 5H_{\text{H}_2(\text{g})}$$

This result indicates that the heat of formation of butane is 53,626 Btu/lb-mole, or 923 Btu/lb, and may be interpreted as meaning that when 4 moles of solid carbon unite with 5 moles of gaseous hydrogen to form 1 mole of gaseous butane, the constant-pressure heat of reaction is 53,626 Btu. The calculation of the heat of formation from the heat of combustion of a fuel compound, as above, or the calculation of the heat of combustion of a compound when its heat of formation is known, is an application of the First Law, as a brief study of the foregoing example will show.

The heat of formation of fuel compounds may be negative as well as positive; for example, the heat of formation for acetylene is  $-3300$  Btu/lb. When negative, the heat of formation indicates that heat is given off as the compound is broken down into its elements.

*Example 19:5.* Calculate  $-\Delta H$  for acetylene. Assume a base temperature of  $77^\circ\text{F}$  and the  $\text{H}_2\text{O}$  in the products to be a liquid.

*Solution.* One mole of  $\text{C}_2\text{H}_2$  contains 24 lb of carbon, 2.016 lb of hydrogen. If burned to  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ , respectively, the constant-pressure heats of combustion of these weights of carbon and hydrogen would total

$$(24)(14,087) + (2.016)(60,958) = 460,979 \text{ Btu}$$

But the heat of formation of  $\text{C}_2\text{H}_2$  is  $-3300$  Btu/lb, or  $-86,000$  Btu/mole. Therefore 86,000 Btu is absorbed in the formation of 1 mole of  $\text{C}_2\text{H}_2$ . According to the First Law, this heat must be added to the heat of combustion of the elements C and H as calculated above to obtain the heat of combustion of the compound, or

$$-\Delta H_{\text{C}_2\text{H}_2} = 460,979 + 86,000 = 546,979 \text{ Btu/mole} = 21,000 \text{ Btu/lb}$$

**19:6. Dissociation.** The direction of the arrow in the basic combustion equations of Art. 19:2 [Eqs. (19:1) to (19:5)] allows the reader to infer that these reactions are unidirectional. At atmospheric, or even considerably above atmospheric, levels of temperature this is practically true, but at high temperatures an increasing tendency toward *dissociation* makes its appearance. Dissociation is the opposite of the combustion reaction and can be represented by the same equation but with the arrow reversed; at very high temperatures molecules may even dissociate into atoms. The First Law will make it clear that, just as the combustion reaction was accompanied by the release of energy, energy will be absorbed during dissociation.

The temperatures with which the engineer deals do not even approach levels at which dissociation is complete, *i.e.*, at which the products of combustion, formed at lower temperatures, are again completely reduced to the reactants through the process of dissociation. In the calorimeters described in Art. 19:4, essentially complete combustion is ensured by the low level of temperature at which the reaction is conducted and by the excess of oxygen for combustion that is always provided. Even in the common open-flame engineering combustion processes that are carried out at considerably higher temperature, as in the furnace of the steam power plant, dissociation is usually a negligible factor in reducing the net amount of energy release. On the other hand, when combustion is carried out in a confined space under high pressure and when the supply of oxygen for combustion is limited, as in the combustion that takes place within the cylinder of the internal-combustion engine, the effects of dissociation assume increased engineering importance.

As the combustion process proceeds, a large part of the energy released is temporarily stored in the products, raising their temperature. As a result of this increase in temperature, the tendency toward dissociation increases, thus slowing down, and finally bringing to a halt, the combustion process before it is completed. When this balance is reached, certain amounts of unburned reactants will remain among the products but the mixture is said to be in *chemical equilibrium*, meaning that it has no further tendency toward either combustion or dissociation.

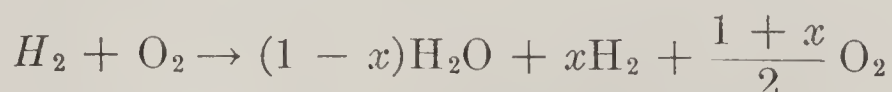
The proportions of fuel that will remain unburned in the products in spite of the presence of oxygen in those products depend upon the temperature and pressure, when the mixture is in chemical equilibrium.<sup>1</sup> It will also depend upon the amount of oxygen supplied as compared with the requirements for complete combustion. These proportions constitute the *most stable state* of the mixture, and the capacity for energy release by the fuel as the result of combustion should be based on this most stable state.

In identifying the most stable state, use is made of a parameter called the *equilibrium constant*, which defines the degree of completeness of the reaction. This equilibrium constant is computed from a formula based

<sup>1</sup> Fuel and air alone may of course be the sole components of a mixture that is in "equilibrium" at atmospheric temperature, or even at levels of temperature considerably above that of the atmosphere. It requires a finite disturbance, such as the creation of a high temperature in a very small part of the mixture, to initiate the reaction and to cause the system to assume a state of chemical equilibrium. The non-chemical equilibrium of the original mixture of fuel and air may be compared to the equilibrium of a block held stationary on an inclined plane under the passive resistance that is offered by static friction. Here again, if the necessary disturbance is supplied, the system will sweep to a state of stable equilibrium. In both cases, the original state is classed as metastable.



on the partial pressures of the reactants and the products in the mixture that results from combustion; for a given reaction it is a function of the temperature. To find the degree of dissociation corresponding to a given temperature in a given reaction, resort is made to a chart from which the value of the constant that corresponds to that temperature and that reaction is read. The reaction equation is then written in terms of an unknown ratio  $x$  which represents the amount of dissociation. For example, in the combustion of hydrogen with 100 per cent excess oxygen, this equation would be written as



Based on this equation, the partial pressures of the gaseous products may be calculated in terms of  $x$ , if these gases are assumed to be perfect gases. An expression for the equilibrium constant, written in terms of  $x$ , can thus be obtained, and, placing this expression equal to the value which has been read from the chart, the value of  $x$  (the degree of dissociation) may be determined; the most stable state corresponding to the given temperature can thus be identified.

The application of this method is attended by complications such as the consideration that the final temperature of the products must be consistent with the amount of energy that can be released in changing to the most stable state. Also, the fuel may contain both carbon and hydrogen, and thus two reactions, instead of one, will be carried out simultaneously; this results in two unknowns instead of one and often causes the computations to be of a trial-and-error nature. A more complete discussion is beyond the scope of this book, and the reader is referred to other texts.<sup>1</sup>

In making a thermodynamic study of the processes through which the working fluid progresses as it passes through an internal-combustion plant, it is essential to locate the most probable state corresponding to the conditions that exist at the beginning and end of each process. If we use the Otto-cycle engine as an example, the state at the beginning of the isentropic compression may be based on the proportions of fuel to air and the pressure and temperature at that point, known or assumed; this is not a most stable state since the temperature is below that required to initiate the combustion reaction.

Nor is the state at the end of the compression a most stable state, but it may be located, if the compression ratio is known or assumed, by apply-

<sup>1</sup> For more detailed discussion of the equilibrium constant, see E. F. Obert, "Thermodynamics," pp. 382-387, McGraw-Hill Book Company, Inc., New York, 1948; J. H. Keenan, "Thermodynamics," pp. 457-465, John Wiley & Sons, Inc., New York, 1941.

ing the assumption that the system is a simple system for the period of the compression and that the compression is isentropic.

During the constant-volume combustion, the working system sweeps to a most stable state which may be located by methods to which reference has already been made. As the products begin their isentropic expansion, the temperature and pressure decrease; the lower temperature corresponds to a lesser degree of dissociation, and there may be some afterburning. However, when the temperature falls below about 1600°F in the course of this expansion, the reaction rate becomes very slow and the products maintain the same ratio of concentration during any further decrease in temperature; the system thus may again depart from a most stable state. The composition of the products at the end of the adiabatic expansion is established, however, and the corresponding state may be located.

Treating the working system as a simple system from this point until the starting point is again reached, the state at the beginning and end of the rest of the processes is located and the operation of the simplified Otto-cycle engine is analyzed; the qualification "simplified" is made since, although this analysis will show the effects of dissociation and will avoid the greater approximations involved in air-standard methods of analysis because of assuming the system to be a simple system throughout the cycle, it makes no allowance for factors such as friction or radiation. Hershey, Eberhardt, and Hottel<sup>1</sup> have constructed combination *ES* and *HS* charts for various fuel-air ratios which are convenient for a rapid solution of problems of this kind. At each level of pressure and temperature, the internal energy and the enthalpy of the most stable state of the products may be read from these charts.

**19:7. The flame temperature** is the highest temperature reached by the gases as the combustion is carried to the most stable state of the products. In the solution of problems in which dissociation is an important factor, much time may be saved if the engineer can make an accurate estimate of the flame temperature that will result.

The easiest, but the most inaccurate, assumption that can be made as the basis of an estimate of flame temperature is that combustion is complete, that the specific heat of the products is constant, and that the combustion process is adiabatic. If the combustion takes place at constant volume, the work, as well as the heat flow, is zero and the internal energy of the products must equal the internal energy of the mixture. But, at the same temperature, these internal energies differ by an amount which we have called the constant-volume heat of combustion and designated as  $Q_v$ .  $Q_v$  must therefore equal  $\Delta U$  for the products as their temperature

<sup>1</sup> R. L. Hershey, J. E. Eberhardt, and H. C. Hottel, "Thermodynamic Properties of the Working Fluid in Internal-combustion Engines," *SAE Journal*, October, 1936, pp. 409-424.



increases to the flame temperature from the temperature at which the reaction began, or

$$\Delta U_{\text{products}} = M_p c_{v_p} (T_2 - T_1)$$

and

$$T_2 - T_1 = \frac{Q_v}{M_p c_{v_p}} \quad (19:16)$$

in which  $T_2$  = flame temperature

$T_1$  = temperature at which reaction began

$M_p$  = mass of products per unit mass of fuel

$c_{v_p}$  = specific heat at constant volume of the products

If the combustion takes place at constant pressure, as in open-flame steady-flow combustion, there is again no work, other than flow work, and, from Eq. (3:5), we see that  $Q_p$  must equal  $\Delta H$  for the products, or

$$T_2 - T_1 = \frac{Q_p}{M_p c_{p_p}} \quad (19:17)$$

in which the meaning of the terms is the same as in Eq. (19:16) except that  $Q_p$ , the constant-pressure heat of combustion, has replaced  $Q_v$  and  $c_{p_p}$ , the specific heat at constant pressure of the products, takes the place of  $c_{v_p}$ .  $Q_p$  differs only in relatively small amount from  $Q_v$ ; it may be larger, smaller, or have the same value. On the other hand,  $c_p$  for the gases in the products is considerably larger than  $c_v$  for those products. It becomes evident that the flame temperature that results from a constant-pressure combustion will be considerably below that resulting when the combustion takes place at constant volume.

In the foregoing analyses, the specific heats have been held constant for simplicity of treatment. If their variation is to be given effect,  $\Delta U = M_p \int_{T_1}^{T_2} c_{v_p} dT$  and  $\Delta H = M_p \int_{T_1}^{T_2} c_{p_p} dT$ . Since  $\Delta U = U_{2\text{products}} - U_{1\text{products}}$  and  $\Delta H = H_{2\text{products}} - H_{1\text{products}}$ , the tables of internal energy and enthalpy which are included in the gas tables may be used to simplify the estimation of flame temperature.

The flame temperatures as calculated by the method described above are highly theoretical and represent a maximum that could conceivably be attained only on the basis of the assumptions which have been made. The engineer makes deductions from this theoretical flame temperature to allow for various factors in arriving at his estimate of a probable actual flame temperature. Some of these factors are listed below:

1. As the flame temperature increases, the effect of dissociation becomes increasingly important. This effect is to reduce the net, or effective, heat of combustion per unit weight of the products and thus to reduce the flame temperature. As has been pointed out above, flame temperatures

tend to be higher for constant-volume combustion, and the effect of dissociation is correspondingly greater.

2. The temperature of the products is above the temperature of the surroundings, and a leakage of heat to the surroundings results. The real combustion is not instantaneous and therefore not adiabatic, as was assumed above. Again the effect is to lower the flame temperature.

3. Because the combustion is not instantaneous and because it takes place in the internal-combustion engine behind a rapidly moving piston, neither constant-volume nor constant-pressure combustion is actually attained in these engines in practice. If the volume increases even slightly during what is nominally a constant-volume combustion, the flame temperature is correspondingly reduced; if, during a "constant-pressure" combustion, the pressure drops off before the reaction is complete, the flame temperature is lowered.

**19:8. Power from Combustion.** The engineer makes use of combustion in the manufacture of power to create a source from which heat may be withdrawn at high temperature to supply the heat engine. It has been pointed out in the introduction to the present chapter that only a portion of the heat of combustion may be delivered at temperatures at which this heat may be efficiently used by the heat engine. In preceding chapters it has been emphasized that, even of the heat which reaches the heat engine, only a portion may conceivably be converted into work. The engineer thus realizes a maximum of only about 30 per cent of the heat of combustion in the form of work.

By returning to Art. 6:10, it may be shown that a far larger work delivery is at least thermodynamically conceivable. In that article it was brought out that the maximum useful work that could be delivered by a system, as it changed between two states in each of which it was in pressure and temperature equilibrium with the atmosphere, was equal to the decrease of the zeta, or Gibbs free-energy, function; to realize this maximum useful work, it was required that the change of state be accomplished reversibly and that heat be exchanged only with the atmosphere.

Essentially, the fuel and air enter the heat engine at the pressure and temperature of the atmosphere; in the limit, the products of combustion reach the same pressure and temperature as they are returned to the atmosphere. If the necessary conditions are observed, the combustion process may therefore conceivably account for a maximum amount of useful work, which is defined by the equation

$$W_{u_{\max}} = Z_1 - Z_2 = (H_1 - T_0 S_1) - (H_2 - T_0 S_2) = H_1 - H_2 - T_0(S_1 - S_2) \quad (19:18)$$

in which the subscript 1 refers to the reactants, 2 to the products, and  $T_0$  is the absolute temperature of the atmosphere. The difference  $H_1 - H_2$



is a maximum if sufficient oxygen is provided for complete combustion and if all of the carbon in the fuel appears in the products as carbon dioxide, all of the hydrogen as  $\text{H}_2\text{O}$ ; this difference is the  $-\Delta H$  of Eq. (19:11), the heat of combustion at constant pressure. The difference  $Z_1 - Z_2$ , measuring the maximum useful work, will therefore approach the heat of combustion at constant pressure as the entropy of the products approaches that of the original mixture.

When the engineer uses combustion merely as a source of heat, he withdraws heat in large amounts from the products at high temperatures and thus fails to meet the conditions under which Eq. (19:18) is applicable. In order to meet those conditions, all operations must be reversible, and heat exchange can take place only with the atmosphere; let us see how these requirements might be satisfied. Consider, for example, a mixture of solid carbon with the amount of oxygen necessary for its complete combustion at the temperature and pressure of the atmosphere. Now let this mixture be isentropically compressed to a temperature high enough so that dissociation will be complete. In the course of this compression, the system will pass through the intermediate temperatures, and if combustion is to be prevented during this operation, some sort of inhibitor, or anticatalyst, must be provided. However, once the temperature at which dissociation is complete is reached, the inhibitor can be removed and there will be no unbalanced tendency for the carbon and oxygen to combine.

The inhibitor having been removed, the mixture is allowed to expand slowly and isentropically. As the temperature drops slightly in the first stage of this expansion, a new most stable state is reached which permits the combustion of a limited portion of the carbon. As the expansion continues to lower and lower and lower temperatures, more and more  $\text{CO}_2$  is formed until, by the time the temperature of the atmosphere has again been reached, combustion is essentially complete, with no unburned carbon left. The ordinary process of combustion is a sweeping change with mounting temperatures which, once started, cannot be reversed, but the combustion described here may be conceived as reversible, since, by recompression, the products can be returned to the form of the reactants over an identical, but reversed, path.

During the original isentropic compression with an inhibitor present, the work of compression was  $E_{0\text{mixture}} - E'_{\text{mixture}}$ , where  $E_{0\text{mixture}}$  is the stored energy of the system as a mixture of the reactants at atmospheric temperature and  $E'_{\text{mixture}}$  is the stored energy of the same mixture of reactants, but at the higher temperature of complete dissociation. For the succeeding isentropic expansion during which combustion takes place, the positive work is  $E'_{\text{mixture}} - E_{0\text{products}}$ , the net work of the double process thus being  $E_{0\text{mixture}} - E_{0\text{products}}$ , or  $-\Delta E_0$ . In the reaction that has been used as an example, the volume of the products and reactants are the

same, and, when a return has been made to the temperature of the atmosphere, the pressure of the atmosphere has also been reached, the products may be directly rejected to the atmosphere, and a fresh charge accepted. Also,  $-\Delta E_0 = -\Delta H_0$ , and, since both processes have taken place without change of entropy,  $W_{u_{\max}} = -\Delta H$ .

For other reactions, the pressure of the system as it reaches the temperature of the atmosphere in its expansion may be above or below the pressure of the atmosphere, according to whether the volume of the products is greater or less than the volume of the reactants at the same pressure and temperature. If the pressure is higher than that of the atmosphere, an isothermal expansion to atmospheric pressure may take place while heat flows reversibly *from* the atmosphere; this will be accompanied by an increase of system entropy so that  $S_2 > S_1$  and the useful work will, as based on Eq. (19:18), slightly exceed  $H_1 - H_2 (= -\Delta H)$ . When the pressure is less than atmospheric pressure at the end of the expansion to atmospheric temperature, an isothermal compression, accompanied by reversible heat flow *to* the atmosphere and a decrease in system entropy, may be used to restore pressure equilibrium; here the maximum useful work will be slightly less than  $-\Delta H$ .

The engineer has an example of a similar method of energy conversion before him in the ordinary lead storage battery. The inhibitor which cancels the tendency toward chemical reaction consists in this device of a difference in electrical potential which is maintained between the reactants. When current is drawn from the battery, this difference is reduced and the necessary reaction takes place to again restore a condition of equilibrium. An important difference between this reaction and its combustion counterpart as described earlier is that the energy transfers in the battery take place at constant temperature, the temperature of the atmosphere.

If an electric cell to control the reaction between carbon and oxygen could be devised, the work obtained from a pound of coal would be greatly increased. For reasons such as his failure to discover a suitable inhibitor and his inability to attain the temperatures equivalent to complete dissociation in the combustion of any important fuel, the engineer has so far been unable to realize the benefits that are indicated as theoretically possible.

### Problems

1. Write relations analogous to Eqs. (19:1a) to (19:1d) but based upon combustion equations (19:2) to (19:5), assuming (a) that the oxygen is supplied as pure oxygen in exactly the right proportion for the combustion and (b) that it is supplied as a part of the ideal amount of air.

2. A gaseous hydrocarbon series has the formula  $C_nH_{n+2}$ , where  $n$  is an integer. Write the balanced combustion equation for this series in terms of  $n$ , assuming (a) that pure oxygen is supplied in the minimum amount for complete combustion, (b) that combustion is complete with the theoretical air, and (c) that it is complete when



10 per cent excess air is supplied. (d) Assume that 90 per cent of the theoretical air is supplied and that no free oxygen, carbon, or hydrogen appears in the products.

3. Work Example 19:2, but assume a coal with the following analysis: C, 65; H, 4; O, 8; S, 1; N, 1;  $\text{H}_2\text{O}$ , 12; ash, 9.

4. In burning octane,  $\text{C}_8\text{H}_{18}$ , an Orsat analysis of the products shows the following percentages:  $\text{CO}_2$ , 11;  $\text{O}_2$ , 2.5; CO, 1. What is the air-fuel ratio? The percentage of excess air?

5. In burning the coal of Prob. 3, an Orsat analysis of the products shows the following percentages:  $\text{CO}_2$ , 11;  $\text{O}_2$ , 8; CO, 1. Assuming the cinder in the ashpit to be 40 per cent unburned carbon, write the combustion equation, and determine the percentage of excess air.

6. Calculate the percentages that would be shown by the Orsat analysis of the products when  $\text{C}_8\text{H}_{18}$  is burned with 10 per cent excess air, if the percentage of CO in the products is 5 per cent of the percentage of  $\text{CO}_2$ .

7. Calculate the constant-pressure heat of combustion of octane when (a) the fuel enters the reaction as a liquid and the water vapor leaves as a liquid, (b) when both are gases, and (c) when the fuel is liquid and the water a gas.

8. Based on the data of Table 19:1 and assuming that the gases formed are perfect gases, calculate the constant-volume heat of reaction of octane(l) at  $77^\circ\text{F}$  when the water vapor formed is entirely condensed.

9. Based on a temperature of  $77^\circ\text{F}$  and assuming that the water in the products is in the form of a gas, the constant-volume heat of combustion of a certain oil is 17,900 Btu/lb. If the composition of the oil may be expressed as  $\text{C}_n\text{H}_{2n}$ , when  $n$  is an integer, calculate the constant-pressure heat of combustion at the same temperature. Assume all gases to be perfect gases, the oil to have negligible volume.

10. Calculate the constant-volume heat of combustion when (a) gaseous octane enters the reaction and the water in the products is a liquid and (b) when the octane enters as a gas but the water leaves the reaction as a gas. The base temperature is  $77^\circ\text{F}$ .

11. Calculate the lower heating value of octane at  $77^\circ\text{F}$ .

12. Work Example 19:4, substituting the coal of Prob. 3.

13. Find the heat of formation of octane.

14. The heat of formation of ethylene ( $\text{C}_2\text{H}_4$ ) is  $-174$  Btu/lb. Find  $Q_p$ , assuming a base temperature of  $77^\circ\text{F}$  and that the water in the products is a liquid.

15. The heat of formation of propane ( $\text{C}_3\text{H}_8$ ) is 1440 Btu/lb. Calculate  $Q_p$ , assuming the standard base temperature and that the water in the products is a liquid.

16. Assuming that combustion is adiabatic and complete, that the specific heat of the products is constant and may be based on Table 9:1, that the water in the products is in the form of a vapor, and that the combustion starts at  $77^\circ\text{F}$ , calculate the theoretical flame temperature when gaseous octane is burned at constant pressure (a) with the theoretical air and (b) with 20 per cent excess air.

### Symbols

$c_p$	specific heat at constant pressure
$c_v$	specific heat at constant volume
$E$	stored energy of a system
(g)	gaseous
$h$	specific enthalpy
$H$	enthalpy of a system
$J$	proportionality factor
(l)	liquid

$m$	molecular weight; weight of 1 mole
$M$	mass of a system
$P$	pressure
$Q$	heat flow
$Q_p$	constant-pressure heat of combustion ( $= -\Delta H$ )
$Q_v$	constant-volume heat of combustion ( $= -\Delta U$ )
(s)	solid
$T$	absolute temperature
$T_0$	absolute temperature of the atmosphere
$U$	internal energy of a system
$v$	specific volume
$V$	volume of a system
$W$	work
$x$	amount of dissociation, a decimal fraction

*Subscripts*

$C$	of carbon
$C_4H_{10}$	of butane
$CO_2$	of carbon dioxide
$H_2$	of hydrogen
$H_2O$	of water
$O_2$	of oxygen
$p$	constant pressure
$T$	constant temperature
$v$	constant volume



## CHAPTER 20

### THE TRANSMISSION OF HEAT

**20:1. Introduction.** Heat has been defined in Chap. 1 as that form of energy which moves from the body at higher temperature to that at lower temperature by reason solely of a temperature difference that exists between them. In intervening chapters we have observed that such "heat transfers" are often necessary in carrying out specific thermodynamic processes. Only casual reference has been made, however, to the apparatus necessary to effect these heat exchanges and none at all to the basic principles which underly the design of a heat exchanger. If the broader definition of the meaning of the word thermodynamics as the study of changes in the form *and the location* of energy is accepted, at least some attention should now be given to these principles.

Heat exchangers are a very important part of the engineering plant. Their first cost and the cost of their operation and maintenance are of great importance to the designer in developing a plan for an efficient installation. Thermodynamically, as we have seen, it is desirable to reduce the irreversibility that always accompanies heat transmission in practice by reducing the temperature interval between the bodies that exchange heat. The cost of heat exchangers increases rapidly with this reduction in temperature differential, and the designer must make a decision as to the economic limit to which compliance with thermodynamic principles may go.

Heat exchange is sometimes accomplished, as in jet condensers and open feedwater heaters, by the direct mixing of warm and cold fluids. Where this method of removing heat from a hot or adding it to a cold fluid can be used, it is most efficient from the standpoint of the size and cost of the apparatus required but, on the basis of the Second Law, also is often accompanied by the maximum thermodynamic irreversibilities. In a more commonly used form of the heat exchanger, the heat is transferred between fluids which are separated by a solid wall, such as the wall of a boiler tube; the heat transferred between the fluids cannot exceed the capacity of the wall for heat transfer, and this capacity is the basis of design for this type of heat exchanger. Examples are found in the air preheater, the surface condenser, and the economizer. This class of heat exchanger, in which the fluids are kept separate, is often the only type that is feasible from the practical engineering standpoint when the fluids

differ in their chemical composition and at least one is to be recirculated through the plant cycle.

Provision for heat exchange may be planned and deliberate and may take place under carefully controlled conditions, as in the boiler and condenser of the power plant. Or the heat exchange may be variable and constitute the load on the plant, as in the design of a plant for heating a building. Here the building acts as a heat exchanger, the heat losses varying in magnitude with weather conditions; the plant must be capable of replacing these losses under the most extreme conditions. A similar example is found in the refrigerating plant, except that the natural flow of heat takes place in the opposite direction in this case; refrigeration plants must be designed with a capacity sufficient to remove these heat gains.

The subject of heat transfer has developed in recent years to the point where space requirements forbid more than a review of basic principles in a text of this character. When the transfer of heat is accomplished by the irreversible mixing of fluids, the engineering problem is usually of the simplest character, the properties of the mixture being computed by equating the energy lost by one fluid to the energy gain of the other. For that reason our attention will be centered on the principles which govern when heat is exchanged between fluids that occupy separate compartments or flow through separate channels; in that case design should be based on a proper balance between the theoretical thermodynamic and the economic factors that enter the specific problem.

The classic method of approaching the study of heat transfer through intervening materials or spaces classifies the transfer of heat as being by *conduction*, by *radiation*, or by *convection*. The meanings of these terms are separately outlined below but, in the form of heat exchanger employed in the engineering plant, the transfer of heat takes place typically through a combination of these methods.

*Conduction.* Heat transfer between a hot and a cold body by conduction requires that the space between them must be occupied by some material substance such as a metal wall; but conduction may take place through fluids, either gases or liquids, as well as through solids. The classic example of conduction, to which the reader has undoubtedly been introduced in elementary texts on physics, is the flow of heat along a metal rod, one end of which is placed in a flame, the other held in the hand. As the end which is placed in the fire receives heat, the rate of random movement of the molecules at that end of the rod is increased; as the result of collisions with molecules farther along the rod, they impart increased momentum to these adjacent molecules, and the temperature gradually increases along the rod until, conceivably, it may become too hot to hold. Neglecting the escape of heat into the surrounding air from



sections of the rod between its two ends (as if these sections had been covered by some sort of shield which prevented the escape of heat at an angle to the rod axis), the time rate at which the temperature will increase at the cold end will depend upon the length of the rod, the differential of temperature between its two ends, and the capacity of the material of which the rod is composed for transferring molecular momentum along its length. This rate of increase of temperature is a measure of the rate of heat transfer along the rod. Eventually it is conceivable that a balanced condition will be attained, after which the temperature at neither end of the rod, nor at any intermediate section, will change. This is a *steady state*, and thereafter the flow of heat will continue at a rate which is independent of time. The design of heat exchangers is normally based on the assumption that a steady state is attained, and our discussions to follow will assume this condition whether that discussion is related to a transfer of heat by conduction, by radiation, by convection, or by a combination of methods.

The rod temperatures that are reached as the steady state is attained will depend upon a number of factors, including not only the capacity of the rod for the transfer of heat by conduction but also the capacity of its hot end for receiving heat from the fire and the ability of the hand, or other external body, at the cold end to retransfer the heat which it receives without further increase of temperature at that end. Based upon the First Law, the rate at which heat escapes at the cold end and the rate at which heat enters at the hot end must both be equal to the time rate of heat transfer by conduction along the rod. This equality constitutes a basic relation in heat-exchanger design.

*Radiation.* Heat may be transferred between two separated bodies even when no material substance fills the space between them; this is called heat transfer by radiation. All bodies radiate heat in the form of an electromagnetic wave motion similar to the waves that transmit light.

Suppose a body to be placed in a vacuum and isolated from all other bodies; the sun of our solar system is an adequate though not entirely accurate example, unless we imagine it as the sole occupant of limitless space. Radiation will take place from the surface of this body in the form of heat and will travel through the surrounding spaces in straight lines, much as a light wave might travel. Now let a second body be introduced into this surrounding space; an obvious example is our own planet, the earth. The earth will also be the source of heat waves into the space that surrounds it. A part of the heat waves from the sun will be intercepted by the earth and, striking its surface, may be reflected or absorbed or may pass through the earth into the space beyond it; the latter effect is negligible in the case of the earth. At the same time, the earth's heat waves are being intercepted at the sun's surface, and an

exchange of energy, though by no means an equal exchange, thus occurs. If we use the earth as our "thermodynamic system," the net amount of heat which it receives by radiation is the difference between the energy carried along the small fraction of the sun's rays which it intercepts and the energy it sends out in similar rays from all of its surface. Because the intensity of heat radiation has been shown to be proportional to the fourth power of the absolute temperature of the surface from which the rays emanate, the earth receives about as much heat by radiation from that part of the sun's rays that it intercepts as it sends out into surrounding space from its entire surface; this balance varies slightly with the season of the year over limited portions of the earth's surface. The net heat flow by radiation is thus almost zero with respect to the system that has been selected.

Returning to the example of the rod that was used in discussing heat transfer by conduction, it is probable that no small part of the heat that flowed into the hot end of the rod was radiated heat. The amount of radiant-heat transfer between two bodies becomes important when the temperature of one of the bodies is high or both temperatures are high but a significant difference in temperature exists between them. In the example, the temperature of the flame is high enough to ensure fairly high intensity of its heat-wave emanations. Of course only a small fraction of these rays are directly intercepted by the rod end and transmitted as conducted heat along the rod. The rod would have received heat by radiation even if it had been removed from direct contact with the flame, but the number of rays it intercepted would have been fewer and the heat transfer proportionately less in this case. Note also that these radiant waves would in this case have passed through a material substance, the air surrounding the rod end. A void is not necessary for the transfer of heat by radiation; some substances, especially the more transparent solids and gases, transmit, rather than absorb or reflect, by far the larger portion of heat rays that they intercept. Thus the temperature of the air, even a very short distance in front of a brick wall on which the sun's rays fall directly, may be considerably below the temperature of the wall surface.

*Convection.* The passage of heat purely by conduction assumes that the two bodies between which heat is exchanged and the intervening wall of material through which that heat must pass have no relative movement with respect to each other. If either body, or the wall between them, consists of a fluid, it is probable that the heat flow will produce differences in temperature, and thus in density, of various sections of the fluid and that relative movement of the layers of fluid will result. When fluid movement occurs in this manner it is called *natural convection*. Often, as when the fluid is pumped or blown through the passages of a heat



exchanger, its movement is directly encouraged and the term *forced convection* is used. In either case, the rate of heat flow by conduction may be considerably affected, and the heat transfer is classified as being by convection. In engineering forms of the heat exchanger, the transfer of heat is typically between fluids and convective effects are of great importance.

As an example of the effect of convection on heat transfer, consider a vertical building wall, as illustrated in Fig. 20:1. The air outside the building, at the lower temperature  $t_o$ , and the air inside, at  $t_i$ , will first be

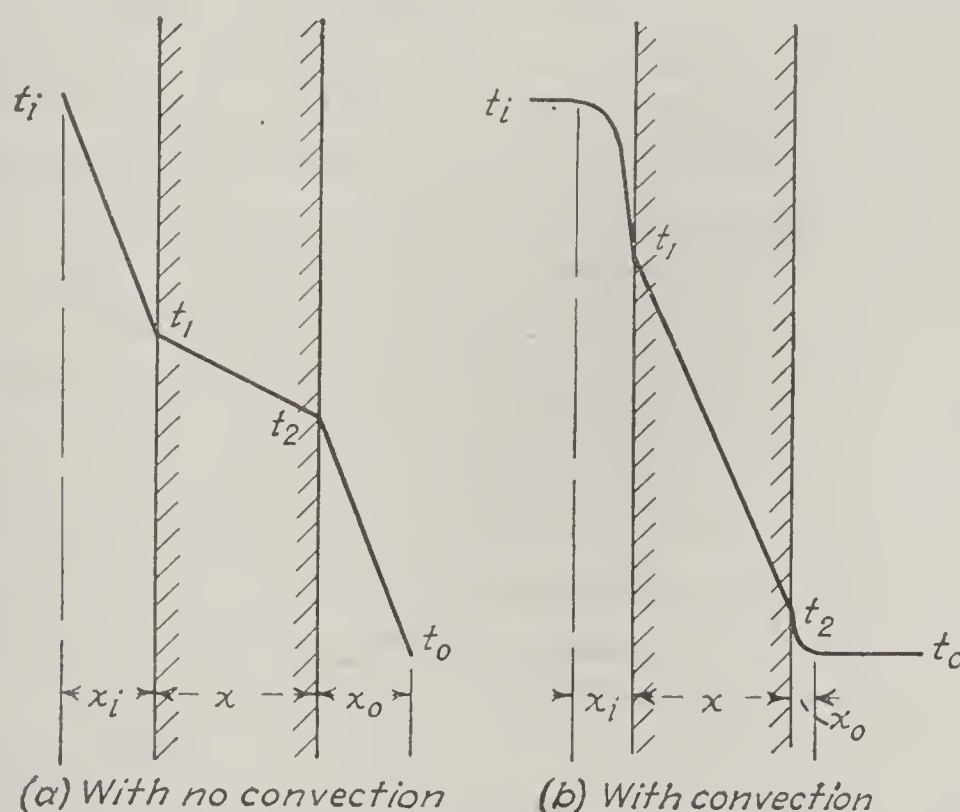


FIG. 20:1. Temperature gradient through a vertical homogeneous building wall.

assumed to be stationary with respect to the wall, with all convective effects eliminated. The temperature of the air outside and inside the wall are both relatively low, and heat flow by radiation is negligible; the sole method of heat transfer is therefore by conduction in the assumed case, which is illustrated in part *a* of the figure. For simplicity, it is assumed that the flow of heat takes place from a vertical layer of air a distance  $x_i$  from the inside surface of the wall and that the temperature of this layer is  $t_i$ . A temperature difference of  $t_i - t_1$  between this layer and the layer of air in immediate contact with the inner wall surface furnishes the incentive for the flow of heat toward the wall. The *temperature gradient* is this temperature difference divided by the distance  $x_i$ , or  $(t_i - t_1)/x_i$ . On the outer side of the wall a temperature gradient  $(t_2 - t_o)/x_o$  accounts for the flow of heat from the wall into the outside air. The slopes of the lines  $t_i t_1$  and  $t_2 t_o$  are graphically representative of the temperature gradients, and these slopes have been shown as equal under the conditions assumed in (a) of Fig. 20:1 since the heat flow

to and from equal inside and outside wall areas must be the same. The heat flow through the wall is also identical per unit of time with the heat flow into its inner and away from its outer surface, and this heat flow is secured by means of the temperature gradient  $(t_1 - t_2)/x$  through the wall. In this connection, it will be noted from the figure that (1) the skin temperatures  $t_1$  and  $t_2$  of the wall have been shown as equal to the temperatures of the air layers in immediate contact with the respective surfaces and (2) the temperature gradient through the solid wall has been shown as much smaller than that which it is necessary to maintain through the air layers in order to produce the same flow of heat by conduction; this means that the solid material of the wall has been supposed to be a better agency for the transfer of heat by conduction than the air on either side and is a natural assumption since the more densely crowded molecules of the wall would appear to be capable of imparting their momentum more rapidly to adjacent molecules, collisions being more frequent.

Now let us introduce the effects of convection, as in Fig. 20:1b. The difference of temperature between the layers of air at  $t_i$  and  $t_1$  will bring about a difference in their densities, and the layer of air in contact with the wall's inner surface will flow downward, the layer at  $t_i$  upward. Thus a circulation will be produced, and the resultant mixing will have a tendency to reduce the temperature difference  $t_i - t_1$ . The assumption made in case *a* would lead us to expect a maximum air temperature at some point near the middle of a room exposed on all four sides, but the circulation that results from convective effects causes a plateau of temperature to be reached at a short distance from the inner wall surface, as is indicated by the leveling off of the temperature-gradient curve at a point very close to the wall. The temperature-gradient curve is no longer of constant slope but has its greatest slope close to the wall. A similar effect is meanwhile being produced by convective effects at the outside wall surface; in this case, the skin temperature of the outside wall surface is lowered. Note in comparing the two figures that the lowering of  $t_2$  has been greater than the temperature range through which  $t_1$  was raised. This is based on the assumption that wind in the outside air will act to increase the convective effects, the air-layer thickness necessary to attain the plateau level of outside temperature being less than the thickness of the similar layer at the inside wall. The effect at the inside wall may be ascribed to natural convection, that on the outside surface may be compared to the forced convection used in many engineering forms of the heat exchanger.

One of the effects of convection has been to increase the temperature gradient through the wall; for the temperature difference  $t_1 - t_2$  is now greater than when no allowance was made for convection. The flow of heat through a unit area of wall surface in unit time is thus increased in



proportion to the increase of this temperature differential. But the heat entering and leaving the wall must also have increased if steady-state conditions are assumed. Accordingly, as has been shown in Fig. 20:1b, the temperature gradient in the air layers immediately adjacent to inner and outer wall surfaces has been increased above the comparable slopes as shown in part *a* of that figure to account for this greater rate of heat flow.

The engineering heat exchanger typically transfers heat between fluids, and the effects of convection, natural or forced, are of corresponding importance in design. The problem of calculating convective heat transfer is much more varied, complicated, and difficult than for either conducted or radiant heat. For the purpose of illustrating the effects of convection, we have here made use of a very simple example. It will occur to the reader that a number of factors will enter the problem and exert their influence in controlling the final result. Among these are, with respect to the solid wall, its length in the direction of convective flow and its inclination to the vertical. With respect to the fluid, some of the important factors are the density, the heat capacity (specific heat), the effect of temperature differences on the density (the coefficient of cubical expansion), the viscosity, and its capacity for conveying heat by conduction. Also to be considered are the temperature difference between fluid and wall and, in the case of forced convection, the velocity of flow.

In conclusion, it should be emphasized that convection is not a basic method of heat transfer, as are conduction and radiation. But the effects of convection are to change, often in radical degree, the rate of heat transfer by conduction. This effect is accomplished by increasing the temperature gradient through both the wall and the immediately adjacent fluid layers. It has been found convenient, however, to handle its discussion separately from the discussion of heat transfer by conduction and radiation.

**20:2. Heat Transfer by Conduction.** The basic equation for heat transfer by conduction follows:

$$Q_{\text{cond}} = kA \frac{dt}{dx} \quad (20:1)$$

in which  $Q_{\text{cond}}$  is the heat transferred per hour across a wall of area  $A$  normal to the direction of heat flow, through a material which has a *thermal conductivity*  $k$ ,\* when the temperature gradient is  $dt/dx$ . No difficulty will be encountered on account of algebraic sign in the use of this equation if it is remembered that the direction of heat flow must always be toward the lower temperature. The units in which each of the terms of Eq.

\* This symbol should not be confused with the ratio  $c_p/c_v$ , also represented by the same letter.

(20:1) are expressed must, of course, be mutually consistent. It is the usual practice, in the English system, to express  $Q_{\text{cond}}$  in Btu per hour,  $A$  in square feet,  $t$  in degrees Fahrenheit, and  $x$  in inches. The unit of measurement of the thermal conductivity  $k$  would then be the number of Btu of heat conducted through a homogeneous wall of the particular material 1 in. in thickness in 1 hr when the differential of temperature across the wall was  $1^\circ\text{F}$ . A unit of thermal conductivity for which the basic wall thickness is 1 ft is also important and is one-twelfth the size of  $k$  as described above, since the resistance offered to the flow of heat is twelve times as great for twelve times the wall thickness. When the conductivity is expressed in terms of this unit, the dimension of  $x$  changes to feet, and the temperature gradient increases in the same proportion so that the same heat flow is calculated. The basic dimension of thermal conductivity is always the same and may be derived from Eq. (20:1) as follows:

$$[k] = \left[ \frac{Q \, dx}{A \, dt} \right] = \frac{[ML^2/\theta^3][L]}{[L^2][T]} = \left[ \frac{ML}{\theta^3 T} \right] \quad (20:2)$$

It will be noted that it has here been convenient to add a fourth basic dimension  $T$ , representing temperature, to the three suggested in Chap. 17.

**20:3. Thermal Conductivity.** Not only solids but also liquids and gases are capable of transferring heat by conduction. The conductivities of homogeneous solid materials are relatively high, tending to increase with their density and their elasticity and, for a specific material, with the temperature and the absorption of moisture. Good insulation against the conduction of heat is provided by solids which are porous, fibrous, or cellular. Values of  $k$  may be obtained from tables similar to Table 20:1. The variation of thermal conductivity of solids with temperature is not ordinarily shown in these tables since their resistance to the flow of heat is usually only a small part of the total resistance encountered by that flow in the engineering heat exchanger. Values of  $k$  vary widely for solids, from a minimum of about 0.3 (Btu) (in.)/(ft<sup>2</sup>)(°F)(hr) for the best insulators to a maximum of around 3000 for the best conductor of heat.

The thermal conductivity of liquids and gases is not as accurately measurable as that of solids because of the difficulty of eliminating convection currents in fluids. A larger variation in experimental results and in tabulated values of  $k$  may therefore be expected. The variation of conductivity with temperature is of greater engineering importance for fluids, especially for gases, and a linear relation between  $k$  and  $t$  is employed; thus

$$k = k_0[1 + C_1(t - t_0)] \quad (20:3)$$



TABLE 20:1. THERMAL CONDUCTIVITIES OF SOME SOLIDS, LIQUIDS, AND GASES\*

Material	$t_0$ , °F	$k_0$ , (Btu)(in.)/ (ft <sup>2</sup> )(°F)(hr)	$C_1$
<i>Solids</i>			
Aluminum.....	32	1000	For solids, use 0
Aluminum, piston alloy.....	400	1200	
Asbestos, corrugated board.....	86	0.84	
Asphalt.....	70	4.8	
Bearing metal, white.....	68	164	
Brass.....	32	590	
Brick, building.....	68	5	
Fire-clay.....	900	7.2	
Cast iron.....	68	350	
Celotex.....	70	0.33	
Concrete, stone.....	...	6.5	
Copper.....	32	2100	
Corkboard.....	86	0.3	
Felt, wool.....	86	0.36	
Glass, window.....	68	6	
Glass wool.....	...	0.27	
Gold.....	64	2028	
Gypsum plaster.....	...	3.3	
Lead.....	64	2400	
Limestone.....	75	6.5	
Magnesia, 85%.....	212	0.47	
Mineral wool.....	86	0.27	
Scale, boiler.....	150	10-20	
Silver.....	32	3200	
Soil, dry.....	95	1.0	
Wet.....	105	4.0	
Steel.....	200	300	
Wallboard, fiber.....	70	0.34	
Plaster.....	86	0.48	
Wood, balsa.....	86	0.36	
Fir and pine.....	...	0.8	
Oak and maple.....	...	1.15	
<i>Liquids</i>			
Ammonia.....	68	4.03	+0.0018
Benzene.....	32	1.02	-0.0028
Brine (NaCl), 25%.....	-4	2.76	+0.0006
Kerosene.....	68	1.04	-0.0009
Mercury.....	32	58	0
Petroleum oil, sp gr = 0.88.....	0	0.94	-0.0003
Sulfur dioxide.....	68	2.3	+0.0003
Water, pure.....	68	4.1	+0.001
Sea.....	68	5.0	
<i>Gases</i>			
Air.....	32	0.163	+0.00165
Ammonia.....	32	0.149	+0.00028
Carbon dioxide.....	32	0.097	+0.0021
Carbon monoxide.....	32	0.155	+0.0017
Hydrogen.....	32	1.13	+0.0015
Nitrogen.....	32	0.168	
Oxygen.....	32	0.170	
Steam.....	32	0.117	+0.00217

\* Adapted from various sources, including International Critical Tables; American Society of Refrigerating Engineers, "Heat Transmission of Building Materials"; W. J. King, *Mech. Eng.*, April, 1932; W. H. McAdams, "Heat Transmission," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942; American Society of Heating and Ventilating Engineers, "Guide."

in which  $k$  is the thermal conductivity at temperature  $t$ ,  $k_0$  at some base level of temperature  $t_0$ , and  $C_1$  is a constant which defines the relative rate of change of conductivity with temperature;  $C_1$  may be positive or negative. Values of  $k_0$ , the corresponding temperature  $t_0$ , and of the constant  $C_1$  are shown for some liquids and gases in Table 20:1.

**20:4. Typical Problems in Heat Transfer by Conduction.** The fundamental problem in the transfer of heat by conduction is the calculation of the heat transferred through a homogeneous plane wall such as that illustrated in Fig. 20:1. A variation of this problem is found when the wall, though bounded by parallel plane surfaces, consists of laminations of materials having different conductivities. Another problem presents itself when the wall is not plane but is curved so that the areas through which the heat enters the wall and leaves it differ; the most common engineering example of this problem is the calculation of the heat flow through the wall of a pipe which carries a thick layer of insulation. Equation 20:1 is applied to these situations below.

*Conduction of Heat through a Homogeneous Plane Wall.* This case is illustrated in Fig. 20:1. Because of the homogeneity of the wall, the temperature gradient will be constant throughout its thickness if any change of  $k$  with temperature is neglected. Then  $dt/dx = (t_1 - t_2)/x$ , where  $t_1$  and  $t_2$  are, respectively, the skin (surface) temperatures of the wall on its warmer and cooler sides and  $x$  is the total thickness of the wall. When  $k$  is in the units of Table 20:1,  $x$  is in inches and the temperature in degrees Fahrenheit. Equation 20:1 applies to a slice of the wall of infinitesimal thickness in the direction of heat flow. For the entire wall, the substitution suggested above gives

$$Q_{\text{cond}} = A \frac{k}{x} (t_1 - t_2) = AC(t_1 - t_2) = A \frac{1}{R} (t_1 - t_2) \quad (20:4)$$

in which the meaning of all terms except  $C$  and  $R$  has already been explained.  $C = (k/x)$  is the *conductance* of the wall; it represents the ability of the wall of thickness  $x$  to conduct heat and, using the system of units we have adopted, is expressed in Btu/(ft<sup>2</sup>)(°F)(hr). The reciprocal of the conductance is the *resistance* which the wall offers to the flow of heat, represented here by the symbol  $R$ .\*

A word of warning must be inserted here. The usual problem with which the engineer deals is the calculation of the heat flow between two fluids on opposite sides of a solid wall. He usually bases his solution of the problem on known or assumed values for the temperatures of these fluids at points removed from the wall surfaces, and the wall skin temperatures  $t_1$  and  $t_2$  cannot properly be assumed equal to the assigned fluid

\* Not, of course, to be confused with the gas constant, designated by the same symbol.



temperatures for reasons which have already been explained in our preliminary discussion of the effect of convection. We shall not be equipped for the solution of the engineering problem in its usual form until we have explored the effects of convection in greater detail; this will be done later in the present chapter.

*Example 20:4A.* A brick building wall 12 in. thick has an inside surface temperature of  $56.3^{\circ}\text{F}$ , an outside surface temperature of  $3.7^{\circ}\text{F}$ . It is 9 ft high and 20 ft long. (a) What is the heat transfer by conduction through this wall per hour? (b) What is its conductance? (c) Its resistance?

*Solution:*

$$k \text{ (Table 20:1)} = 5; A = (9)(20) = 180; x = 12$$

$$(a) Q = A \frac{k}{x} (t_1 - t_2) = 180 \left( \frac{5}{12} \right) (56.3 - 3.7) = 3940 \text{ Btu/hr}$$

$$(b) C = \frac{k}{x} = \frac{5}{12} = 0.417 \text{ Btu}/(\text{ft}^2)(^{\circ}\text{F})(\text{hr})$$

$$(c) R = \frac{1}{C} = 2.4 \text{ (ft}^2)(^{\circ}\text{F})(\text{hr})/\text{Btu}$$

*Conduction of Heat through a Laminated Plane Wall.* This problem is illustrated in Fig. 20:2. The three laminations are numbered from the left in the figure, and each, separately, consists of a homogeneous plane wall. Thus the resistance of the first lamination is  $x_1/k_1$ , of the second  $x_2/k_2$ , and of the third  $x_3/k_3$ . These resistances may be added to obtain the resistance to the flow of heat by conduction through the complete wall, or

$$R = R_1 + R_2 + R_3 = \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} \quad (20:5)$$

or

$$C = \frac{1}{R} = \frac{1}{\frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3}} \quad (20:6)$$

The value of  $C$  obtained in this manner may be substituted in Eq. (20:4), with  $t_1$  and  $t_2$  of that equation substituted as the extreme surface temperatures of the composite wall, to obtain the heat flow by conduction. Any number of laminations may be handled in this manner.

The rate of heat flow through each lamination is the same when steady-state conditions have been attained, and we may write

$$Q = AC(t_1 - t_4) = A \frac{k_1}{x_1} (t_1 - t_2) = A \frac{k_2}{x_2} (t_2 - t_3) = A \frac{k_3}{x_3} (t_3 - t_4)$$

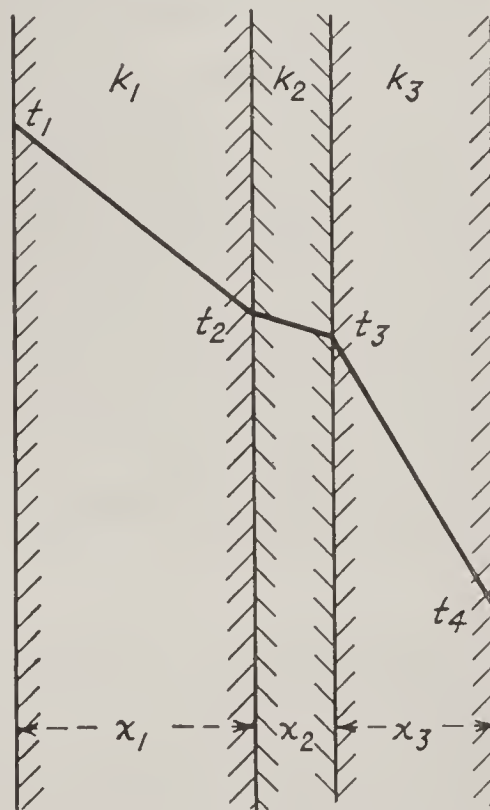


FIG. 20:2. Heat transfer by conduction through a laminated plane wall.

or

$$\frac{t_1 - t_4}{k_1/x_1} = \frac{t_1 - t_2}{C}$$

If  $t_1$  and  $t_4$  are known or assumed,  $t_2$  may be calculated from this proportion. By setting up similar proportions, all interior skin temperatures may be calculated and a line drawn to show the temperature gradient through each lamination, as in the figure.

Sometimes a type of composite wall is employed in engineering construction in which the surfaces of one or more of the laminations is not planar, the lamination thus being of variable thickness; one of the most commonly met examples is the lath-and-plaster wall. For standard types of construction such as this, tests are made of the wall as a whole, and its conductance is reported in tables. Thus for the standard wall of gypsum plaster on wood lath, having a thickness of approximately  $\frac{3}{4}$  in., these tables give a conductance of 2.5. This is equivalent to the ratio  $k/x$  for this wall and may be substituted for it in Eqs. (20:4) to (20:6).

Occasionally one of the inner laminations may consist of a fluid; this is especially true of building walls, often constructed with internal air spaces. Unless the air in this space is confined in small cells to prevent convection, as, for example, when the space is filled with mineral wool, convective effects will enter the problem and cause the temperature gradient to be greater in the fluid laminations near the boundary surfaces of the air space. The methods discussed above should properly be changed to take this factor into consideration. The accuracy required in the engineering calculation is often not extremely close, and sometimes the conductance of such air spaces is expressed in tables and used thereafter as  $k/x$  for the layer of air; these conductances will depend upon the thickness of the air space. This method is, of course, practical only for standardized types of construction but considerably simplifies the engineering calculation.

*Example 20:4B.* A building wall consists of fir siding and sheathing with a combined thickness of 1.62 in., 2- by 4-in. studs, and wood lath and plaster. The  $3\frac{1}{2}$ -in. space between the lath and plaster and the sheathing is filled with mineral wool. Calculate (a) the conductance of this wall, (b) the heat flow per square foot by conduction when the inside surface of the plaster is at  $67.3^\circ\text{F}$  and the outside surface of the siding at  $0.7^\circ\text{F}$ , and (c) the temperature in the center of the space that is filled with mineral wool.

*Solution:*

$$(a) \ C = \frac{1}{\frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{1}{C_3}} = \frac{1}{\frac{1.62}{0.8} + \frac{3.5}{0.27} + \frac{1}{2.5}} = 0.065$$

$$(b) \ Q = (1)(0.065)(67.3 - 0.7) = 4.34 \text{ Btu}/(\text{ft}^2)(\text{hr})$$

$$(c) \ t_2 = \text{temp of inner surface of mineral wool}; t_3 = \text{temp of its outer surface}$$



$$\frac{67.3 - 0.7}{2.5} = \frac{67.3 - t_2}{0.065} \text{ or } t_2 = 65.7^\circ\text{F}$$

$$\frac{67.3 - 0.7}{0.8/1.62} = \frac{t_3 - 0.7}{0.065} \text{ or } t_3 = 9.5^\circ\text{F}$$

Averaging  $t_2$  and  $t_3$  to obtain the temperature at the center of the space, this temperature is calculated as  $37.6^\circ\text{F}$ .

*Conduction of Heat through a Thick Homogeneous Cylindrical Wall.* This case is illustrated in Fig. 20:3. The inner and outer surfaces have radii, respectively, of  $r_i$  and  $r_o$ , the inner skin temperature being  $t_1$  and the outer  $t_2$ . Assuming that  $t_1 > t_2$ , the flow of heat is radially outward, and the area  $A$  for heat flow that enters into Eq. (20:4) changes as the flow proceeds from inner to outer wall; it is in handling this change in area that our problem differs from the two previously discussed.

The entire wall may be divided into annular sections having an infinitesimal thickness  $dr$  such as that shown at a distance  $r$  from the center of the cylinder. The areas of the inside and outside surfaces of one of these annular segments, per unit length of cylinder axis, differ only infinitesimally, and the heat flow through each of them is the same under steady-state conditions; for this homogeneous wall  $k$  is also the same for each. Applying Eq. (20:1) to one of these annular segments over a unit length in the direction of the cylinder axis,

$$dr = \frac{kA \, dt}{Q} = \frac{k(2\pi r) \, dt}{Q}$$

or

$$\frac{dr}{r} = \frac{2\pi k}{Q} dt$$

in which  $dr$  has replaced  $dx$  of Eq. (20:1) and  $Q$  is the heat transfer per unit length of cylinder per hour. Note that, for consistency,  $k$  is expressed in  $(\text{Btu})(\text{ft})/(\text{ft}^2)(^\circ\text{F})(\text{hr})$ . Integrating between limits suggested by the boundary conditions at the inner and outer surfaces,

$$\int_{r_i}^{r_o} \frac{dr}{r} = \frac{2\pi k}{Q} \int_{t_1}^{t_2} dt$$

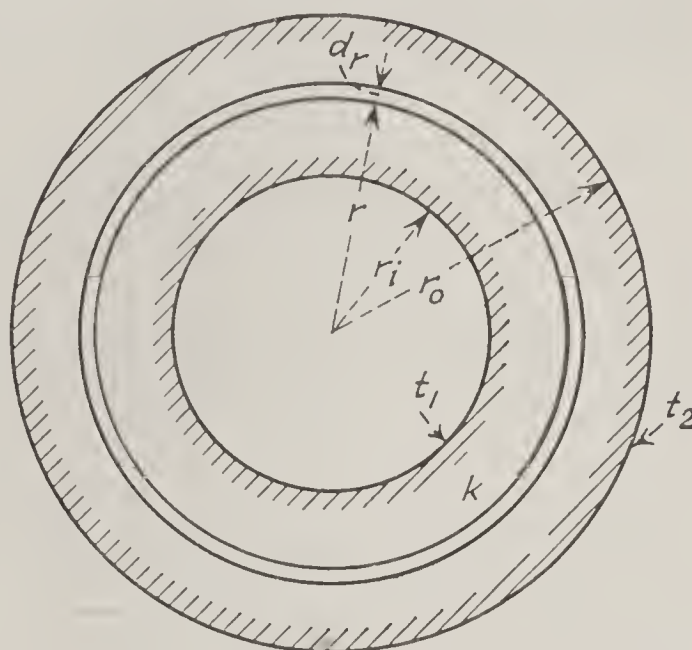


FIG. 20:3. Heat transfer by conduction through a thick cylindrical wall.

or

$$\log_e \frac{r_o}{r_i} = \frac{2\pi k}{Q} (t_2 - t_1)$$

and

$$Q = \frac{2\pi k(t_2 - t_1)}{\log_e (r_o/r_i)} \quad [k \text{ in } (\text{Btu})(\text{ft})/(\text{ft}^2)(^\circ\text{F})(\text{hr})] \quad (20:7)$$

It will be observed that, under the assumption made in attacking this problem (that  $t_1 > t_2$ ), the heat flow from Eq. (20:7) is negative and the fluid within the tube constitutes the "thermodynamic system" to accord with conventions as to the sign of heat flow previously adopted. If the

opposite is the case, it is necessary only to reverse the sign of  $Q$ .

*Conduction of Heat through a Laminated Cylindrical Wall.* One of the principal engineering examples of radial heat flow through a cylindrical wall is found when a hot or a cold fluid flows within a metal pipe which is surrounded by thick layers of insulation. This type of problem is illustrated in Fig. 20:4. The inner shell of material having a conductivity  $k_1$  extends between radii  $r_1$  and  $r_2$ , and its surface temperatures are  $t_1$  and  $t_2$ , as shown. The ma-

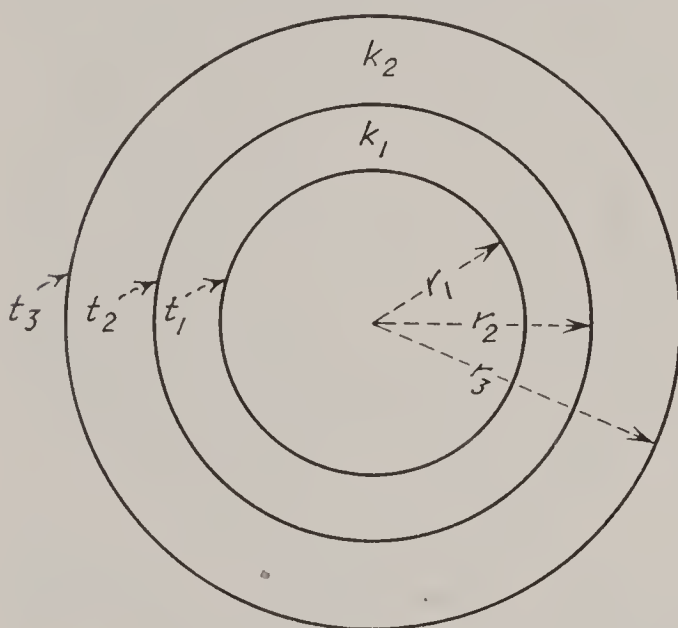


FIG. 20:4. Heat transfer by conduction through a laminated cylindrical wall.

terial of the outer shell has a conductivity of  $k_2$  and extends from  $r = r_2$  to  $r = r_3$ , with surface temperatures similarly notated. Under steady-state conditions, the heat flow rate through both shells is the same, or

$$Q = \frac{2\pi k_1(t_2 - t_1)}{\log_e (r_2/r_1)} = \frac{2\pi k_2(t_3 - t_2)}{\log_e (r_3/r_2)}$$

or

$$t_2 - t_1 = \frac{Q \log_e (r_2/r_1)}{2\pi k_1} \quad \text{and} \quad t_3 - t_2 = \frac{Q \log_e (r_3/r_2)}{2\pi k_2}$$

Then

$$t_3 - t_1 = (t_2 - t_1) + (t_3 - t_2) = \frac{Q}{2\pi} \left[ \frac{\log_e (r_2/r_1)}{k_1} + \frac{\log_e (r_3/r_2)}{k_2} \right]$$

and

$$Q = \frac{2\pi(t_3 - t_1)}{\frac{1}{k_1} \log_e \frac{r_2}{r_1} + \frac{1}{k_2} \log_e \frac{r_3}{r_2}} \quad (20:8)$$



This equation may be extended to apply to any number of cylindrical laminations in an obvious manner. Values of the conductivity are expressed in (Btu)(ft)/(ft<sup>2</sup>)(°F)(hr) in substituting in Eq. (20:8).

**Example 20:4C.** A steel pipe with an outside diameter of 4.5 in. and a wall thickness of 0.25 in. is covered with a 2-in. thickness of 85 per cent magnesia. The surface temperature on the inside of the pipe is 300°F, on the outside surface of the insulation is 90°F. (a) What is the heat flow per hour per foot of pipe length? (b) What is the temperature at the outer surface of the steel pipe? (c) Based on its inside surface area, what is the conductance of the pipe and insulation?

*Solution:*

(a) Let  $k_1$  denote the conductivity of steel and  $k_2$  that of the insulation. Also,  $r_1$  = inner radius of steel pipe,  $r_2$  = its outer radius, and  $r_3$  = outer radius of insulation. Then, from Eq. (20:8),

$$Q = \frac{6.28(90 - 300)}{\frac{12}{300} \log_e \frac{2.25}{2.00} + \frac{12}{0.47} \log_e \frac{4.25}{2.25}} = \frac{-1321}{0.0047 + 16.27} = -81.2 \text{ Btu/(ft)(hr)}$$

(b) Substituting this value of  $Q$  in Eq. 20:7 and applying it to the steel pipe,

$$-81.2 = \frac{(6.28)(300)(t_2 - 300)}{12 \log_e (2.25/2.00)} \text{ or } t_2 = 299.94^\circ\text{F}$$

(c) The inside diameter is 4 in. The inside area per foot of pipe length is  $4\pi/12 = 1.05 \text{ ft}^2$ . From Eq. (20:4),

$$C = \frac{Q}{A(t_1 - t_3)} = \frac{81.2}{1.05(300 - 90)} = 0.369 \text{ Btu/(ft}^2\text{)(}^\circ\text{F)(hr)}$$

**20:5. Heat Transfer by Radiation.** Reviewing the earlier brief discussion of the nature of radiated heat, it is noted that the following points were made:

1. All bodies radiate heat in the form of an electromagnetic wave motion similar to that which carries light.
2. The intensity of these waves (the amount of energy radiated from the body) is proportional to the fourth power of the absolute temperature of the surface from which they issue.
3. A second body, intercepting some of these rays, may absorb, reflect, or transmit the energy carried along them.
4. The perfect transmitter of radiant-heat energy is a void; the ability of matter, whether solid or fluid, to transmit the wave motion tends to increase with the transparency of the material body.

Some elaboration is desirable at this point. The distinction between the wave that carries heat and that along which light is transmitted is found in its wave length. The heat waves occupy a band of wave lengths that lies between the wave lengths of light and the wave lengths of radio, being longer than the former, shorter than the radio waves; there is some

overlapping of these bands, especially between the heat and the light waves. The heat wave obeys the same laws as the light wave, including the laws of reflection and refraction.

The total amount of heat radiated from a body is a function not only of the fourth power of the absolute temperature of its surface but also of the area of its surface and of a property of the body called its emissivity, denoted by the symbol  $\epsilon$ . This emissivity may be changed by changing the nature of the surface of the body; in general, it may be increased by covering the surface with a dull black coating, as by the use of lampblack. The highest value that  $\epsilon$  may have is 1; this value is assigned to a hypothetical *black body* having maximum emissive properties. The emissivities of *nonblack* bodies express their relative emission of radiant heat in comparison with that of a black body. The wave length corresponding to the heat-wave emanations from a black body is that corresponding to maximum intensity of heat transfer; it will vary inversely in length with the absolute temperature of the radiating surface. Emanations from bodies at higher temperatures are therefore characterized by shorter wave lengths, closer to those of the light band or even encroaching upon them.

Of all the radiant-heat rays intercepted by a body, a part will be absorbed and will become, at least temporarily, stored thermal energy in that body; a part will be reflected into the space surrounding the body, and, based on the First Law, account must be made for the balance as having been transmitted through the body into the space beyond it. Most solids (an important engineering exception is glass in thin panes) permit the transmission of a negligible portion of the heat rays that fall on them. This is also true of liquids, but, for most gases, the portion transmitted is very large; thus the air of our atmosphere allows the major portion of the radiant heat from the sun to reach the solid surface of the earth. Opaque bodies having smooth, polished surfaces, light in color, are the best reflectors of the radiant-heat wave. The temperature of the surface of a mirror, held normal to the sun's rays, is far below the surface temperature of a brick wall similarly placed with respect to those rays; since neither transmits an appreciable portion of the rays, much of the difference must be ascribable to the relative amounts of energy reflected and absorbed.

Usually of greatest importance to the engineer, in making calculations that have to do with the transfer of heat by radiation, is the absorptivity  $a$  of the surface that intercepts the radiant-heat rays. The best absorber is the hypothetical black body, which has the highest emissivity, and the value of 1 is assigned to  $a$  for a black body, the absorptivity of nonblack bodies being compared with the standard so set. Since the black body absorbs all of the radiant-heat energy falling upon its surface, reflecting or transmitting none of the rays,  $a$  also represents the portion of the total



radiant-heat energy received which is absorbed. Exactly the same characteristics which make a surface a good emanator of radiant heat cause it to be a good absorber, and the value of  $a$  for the nonblack body is therefore equal to  $\epsilon$  for that body. Accordingly, a known value of either for a specific surface may be substituted for the other. This equality of  $a$  and  $\epsilon$  is based on Kirchhoff's law.

**20:6. The Stefan-Boltzmann equation** evaluates the heat radiated from a black body in terms of its radiating area (in the case of a smooth spherical body, this radiating area is the surface area) and its absolute temperature,

$$Q_{\text{rad}} = \sigma A T^4 \quad (20:9)$$

where  $\sigma$  is a constant, known as Stefan's constant, having a value of  $17.3 \times 10^{-10}$  when  $A$  is given in square feet,  $T$  in degrees Rankine, and  $Q_{\text{rad}}$  in Btu per hour.

The engineer is often less concerned with the total radiant-heat emanating from a body than he is with the portion of that heat which is absorbed by a second body, which happens to constitute the thermodynamic system on which his attention is centered. If that second body is totally enclosed within a radiating surface, it must absorb all of the energy which emanates from that surface. Therefore, no matter what the character of its surface, it becomes a black body in respect to its absorptivity. *A totally enclosed body is a black body.*

In the meantime, of course, the enclosed body is the source of radiant-heat waves of its own, and, until a steady state is reached at which its temperature is equal to that of the surface which surrounds it, there will be a net heat exchange between the two. Remembering that the enclosed body is a black body, the Stefan-Boltzmann equation may be applied to measure this net heat exchange as

$$Q_{\text{rad}} = \sigma A_1 (T_2^4 - T_1^4) \quad (20:10)$$

in which the subscript 1 refers to the enclosed body, 2 to the surrounding surface. With respect to the sign of  $Q$ , the equation has here been written on the assumption that the enclosed body is the thermodynamic system.

When the enclosure is not complete, all of the radiant heat from a radiating source may not be intercepted by the thermodynamic system for which the engineer desires to determine the net radiant-heat transfer. Nor are the emissivities and absorptivities of either body necessarily those of the black body, as in the case represented by Eq. (20:10). That equation must then be modified to take these factors into consideration; the new form is

$$Q_{\text{rad}} = \sigma A_1 F_e F_c (T_2^4 - T_1^4) \quad (20:11)$$

in which  $F_e$  is an *emissivity factor*, depending on the emissivities of the two

TABLE 20:2. CONFIGURATION AND EMISSIVITY FACTORS FOR VARIOUS RELATIONS BETWEEN SOLID SURFACES\*  
(Use in conjunction with Eq. 20:11. Subscript 1 refers to enclosed body)

Item	Surface relations	Area used, $A$	Configuration factor, $F_c$	Emissivity factor $F_e$
1	Infinite parallel planes	Either	1	$\frac{1}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$
2	Completely enclosed body without depressions and small compared with enclosure	$A_1$	1	$\epsilon_1$
3	Completely enclosed body, large compared with enclosure	$A_1$	1	$\frac{1}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$
4	Concentric spheres or infinite cylinders	$A_1$	1	$\frac{1}{\frac{1}{\epsilon_1} + \frac{A_1}{A_2} \left( \frac{1}{\epsilon_2} - 1 \right)}$
5	Direct radiation between parallel and equal squares or disks of width $D$ and distance apart $L$	Either	Fig. 20:5, curves 1 and 2	$\epsilon_1 \epsilon_2$
6	Same as 5, except planes connected by nonconducting and reradiating walls (openings through furnace walls)	Either	Fig. 20:5, curves 3 and 4	$\epsilon_1 \epsilon_2$
7	Same as 6 for slots, $D =$ width	Either	Fig. 20:5, curve 4	$\epsilon_1 \epsilon_2$
8	Two equal rectangles in parallel planes, directly opposite each other	Either	$(F_c' \times F_c'')^{\frac{1}{2}}$ $F_c' = F_c$ for squares (Fig. 20:5) equivalent to smaller side of rectangle. $F_c'' = F_c$ for squares (Fig. 20:5) equivalent to larger side of rectangle. Use curve 2	If $A$ is small compared with $L$ , use $\epsilon_1 \epsilon_2$ . If $A$ is large compared with $L$ , use $F_e$ , item 3
9	Two rectangles with a common side in perpendicular planes	Either	Fig. 20:6	$\epsilon_1 \epsilon_2$

\*Adapted from Croft, as based on Hottel.



TABLE 20:3. TOTAL NORMAL EMISSIVITIES AND ABSORPTIVITIES\*

Material	Temperature of radiating or absorbing body, °F <i>S</i> = solar radiation	Emissivity $\epsilon$ or absorptivity <i>a</i>
Aluminum, oxidized.....	100–1000	0.11–0.18
Polished.....	100–1000–3000	0.04–0.08–0.17
Brick, building, cream.....	<i>S</i>	0.38
Red.....	<i>S</i>	0.70
Fire clay.....	2500	0.75
Refractory, black or chrome.....	200–1000–2000	0.92–0.97–0.98
White or light buff.....	200–1000–2000	0.91–0.65–0.33
Concrete.....	2500– <i>S</i>	0.63–0.65
Copper, polished.....	100–1000–2000	0.04–0.18–0.17
Glass.....	100	0.90
Ice.....	100	0.63
Iron, galvanized, dirty.....	<i>S</i>	0.89
Limestone.....	100	0.95
Marble.....	100	0.56
Oak, planed.....	100	0.91
Paint, aluminum.....	100	0.65
Bronze.....	100	0.51
Smooth white.....	<i>S</i>	0.20–0.40
Black.....	200–600–1000	0.92–0.95–0.97
Red.....	200–600–1000	0.95–0.95–0.85
Green.....	200–600–1000	0.93–0.90–0.80
Paper, asbestos.....	100	0.93
Roofing.....	70	0.91
White.....	100– <i>S</i>	0.80–0.28
Pigments, lampblack.....	125– <i>S</i>	0.96–0.97
Black lacquer.....	125	0.80
White enamel.....	125	0.92
Dark varnish.....	125	0.89
Plaster, rough lime.....	100	0.91
Steel, polished.....	100–1000– <i>S</i>	0.07–0.14–0.45
Oxidized.....	100–1000	0.79–0.79
Water.....	100	0.95

\* From Huber O. Croft, "Thermodynamics, Fluid Flow, and Heat Transmission," McGraw Hill Book Company, Inc., New York, 1938.

bodies and, in some cases, their relative surface areas for radiation and absorption;  $F_c$  is a *configuration factor* which expresses the effect of the relative position of the two surfaces on the average angle of incidence at which the thermodynamic system receives the radiant-heat waves of the other body. For an enclosed body, or for two parallel plane surfaces of infinite extent,  $F_c$  is 1 since the rays are, on the average, normal to both surfaces. The maximum value which either of these two factors,  $F_e$  or  $F_c$ , may have is 1. Table 20:2, in combination with Figs. 20:5 and 20:6,

gives the basis of calculation of  $F_e$  and  $F_c$  for radiating and absorbing solid surfaces disposed in various manners. Table 20:3 presents the emissivi-

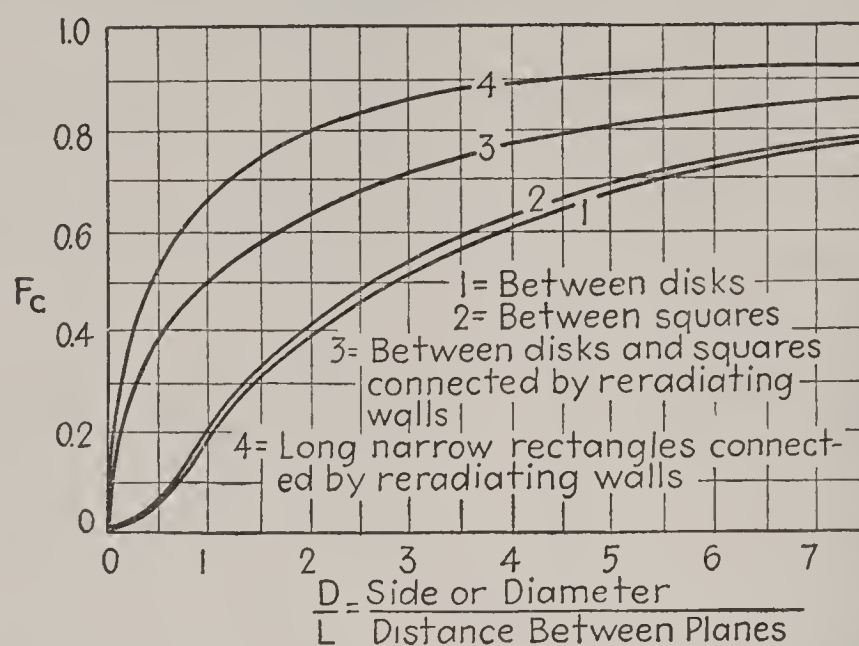


FIG. 20:5. Configuration factors  $F_c$  for parallel surfaces (see Table 20:2).

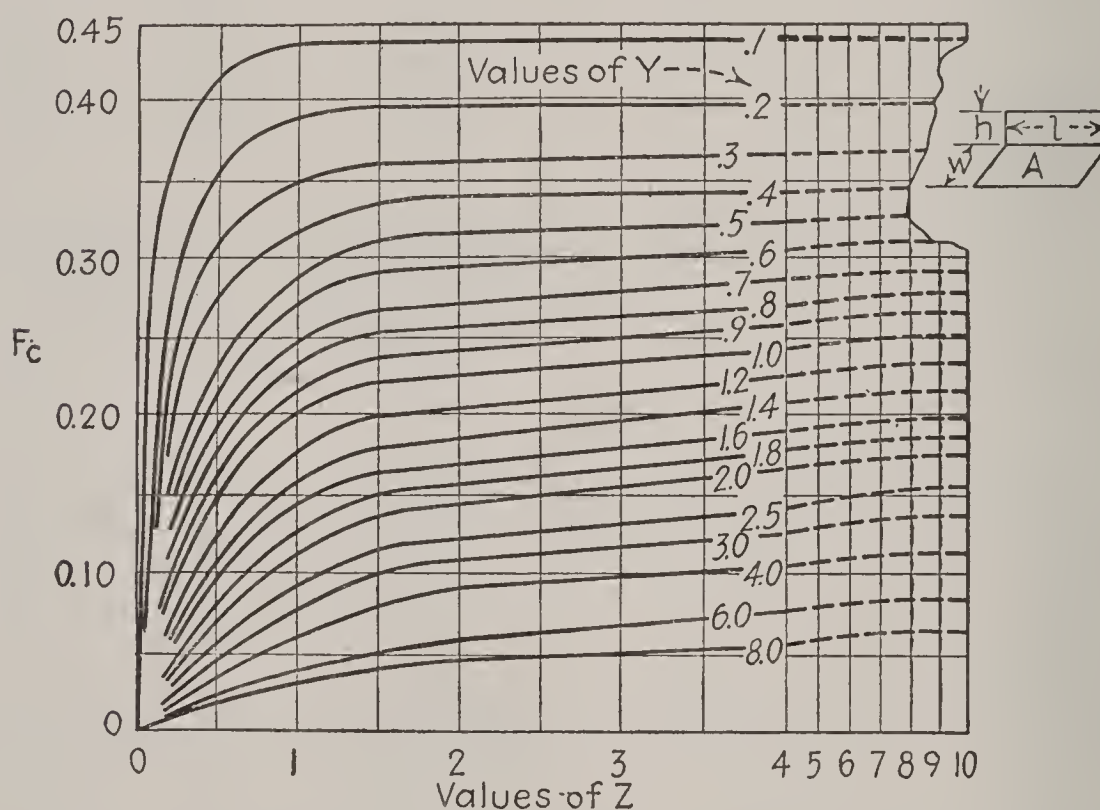


FIG. 20:6. Configuration factors  $F_c$  for radiation between adjacent rectangles in perpendicular planes.  $Y$  = ratio of length of unique side of area presented by the "thermodynamic system" divided by length of the side common to the two rectangles ( $=w/1$ ).  $Z$  = ratio of length of unique side of other rectangle divided by length of the common side ( $=h/1$ ).

ties and absorptivities of various surfaces, showing, when appropriate, the variation of emissivity with surface temperature.<sup>1</sup>

In the engineering problem, the thermodynamic system is almost invariably the body at lower temperature. A case in point is the calcula-

<sup>1</sup> These tables and charts are adapted from Huber O. Croft, "Thermodynamics, Fluid Flow, and Heat Transmission," McGraw-Hill Book Company, Inc., New York, 1938.



tion of the radiant heat received by a surface, such as a building wall, as the result of exposure to the rays of the sun. A surface held normal to the direct rays of the sun at the surface of the earth will, on a clear day, receive about 300 Btu/(ft<sup>2</sup>)(hr) in heat radiation from the sun. When the surface is inclined to the sun's rays, the amount of heat received is less and may be estimated by multiplying 300 by the sine of the average angle which the sun's rays make with the surface. As has been explained above, a part of this heat will be reflected, a part transmitted, and the rest absorbed. For surfaces used in building construction, with the exception of clear panes of glass, the proportion transmitted is negligible; for clear glass panes, nearly all is transmitted. The proportion absorbed is, of course, the absorptivity (or emissivity, since the two are equal) of the surface; Table 20:3 shows, for appropriate surfaces, the emissivities under solar radiation.

*Example 20:6A.* A rectangular 12- by 16-ft furnace has side walls 10 ft high. One of the 16-ft vertical walls is completely obscured by water tubes having a surface temperature of 500°F. The other side walls are of light buff refractory brick and have a surface temperature of 2200°F. Calculate the radiant heat received by the tube bank (*a*) from each of the adjacent vertical walls and (*b*) from the opposite vertical wall.

*Solution:*

(*a*) This corresponds to item 9 of Table 20:2.  $A_1 = 16 \times 10 = 160$  ft<sup>2</sup>. From Table 20:3,  $\epsilon_1$  (oxidized steel) = 0.79;  $\epsilon_2 = 0.33$ . Entering Fig. 20:6 with  $Y = \frac{1.6}{1.0} = 1.6$  and  $Z = \frac{1.2}{1.0} = 1.2$ , read  $F_c = 0.155$ .  $F_e = \epsilon_1 \epsilon_2 = (0.79)(0.33) = 0.261$ .

Substituting in Eq. (20:11),

$$Q_{\text{rad}} = (17.3 \times 10^{-10})(160)(0.261)(0.155)(2660^4 - 960^4) = 550,000 \text{ Btu/hr}$$

Total for the two adjacent side walls, 1,100,000 Btu/hr

(*b*) Item 8, Table 20:2 applies.  $A_1 = 160$  ft<sup>2</sup>. Entering Fig. 20:5 with  $D/L = \frac{1.0}{1.2} = 0.833$ ,  $F_c' = 0.18$  (curve 2). Entering this figure with  $D/L = \frac{1.6}{1.2} = 1.33$ ,  $F_c'' = 0.30$  (curve 2).

$$F_c = (0.18 \times 0.30)^{\frac{1}{2}} = 0.232$$

Area  $A$  is large compared with  $L$ . Therefore, from item 3, Table 20:2,

$$F_e = \frac{1}{1/0.79 + 1/0.33 - 1} = 0.303$$

Substituting in Eq. (20:11),

$$Q_{\text{rad}} = (17.3 \times 10^{-10})(160)(0.303)(0.232)(2660^4 - 960^4) = 950,000 \text{ Btu/hr}$$

*Example 20:6B.* Calculate the total radiant heat absorbed per hour by a building wall 100 ft<sup>2</sup> in area on which the sun's rays fall at an angle of 70°. The exposed surface of the wall is of red brick.

*Solution:*

$$Q_{\text{rad}} = (100)(300)(0.70) \sin 70^\circ = 20,400 \text{ Btu/hr}$$

**20:7. Radiant-heat Transmission of Gases.** The best medium for the transmission of radiant heat is a complete void. In discussing the transfer of radiant heat between solid surfaces, no attention has been given in most cases to the intervening gaseous material that always occupies at least a part of the space between those surfaces in practice. The data on solar radiation are an exception; the stated value of  $300 \text{ Btu}/(\text{ft}^2)(\text{hr})$  at the earth's surface makes an allowance of  $100 \text{ Btu}/(\text{ft}^2)(\text{hr})$  for radiant heat absorbed by the earth's atmosphere as the sun's rays pass through it, the total received at the outer surface of the atmosphere being some  $400 \text{ Btu}/(\text{ft}^2)(\text{hr})$ . Almost all of this difference is absorbed by the carbon dioxide and the water vapor in the atmosphere, the latter being the more important of the two in contributing to this effect.

Heat transfer by radiation is also of maximum importance in the design of the furnaces used in industry to serve as the source of heat supply to the thermodynamic cycle. At least a part of the interior surface of these furnaces is often covered with some refractory material which has the ability to resist destruction at high temperature. Other surfaces, such as banks of tubes, may be designed to transmit heat by conduction directly to the working fluid. These surfaces receive heat from the hot gases by conduction, aided by convective effects, and by radiation; when a surface is "in sight" of the flames in the furnace, the transfer by radiation is usually much greater than by conduction. The refractory-covered surfaces are backed by thermal insulation so that almost none of the heat that reaches them escapes to the surrounding atmosphere; nearly all is either immediately reflected back into the furnace spaces or is temporarily absorbed, creating a high surface temperature so that the refractory becomes a source of high-intensity radiant-heat waves of its own. This reradiation of heat back into the furnace spaces leads to higher temperatures in these spaces and thus to more complete combustion of the fuel. Above a certain limit which is controlled by the characteristics of the fuel, the method of mixing fuel and air, and the method of ash disposal, a further increase of furnace temperature is not desirable. Furnace temperatures may be controlled by using surfaces around a part of the furnace periphery which are not refractory but pass the heat which they receive directly into the working fluid; an example is the tube bank to which reference has been made above. The heat which these metal tubes absorb is almost all passed directly on into the fluid that passes through them; they are thus kept at a level of temperature far below the firebox temperature, and their destruction is avoided. Because of their relatively low temperature, they reradiate a negligible proportion of the heat which they receive either directly from the furnace gases or by reradiation from refractory furnace walls through those gases. Of the heat reradiated toward these cooler surfaces by refractory-covered furnace walls, a part will be absorbed



by the furnace gases; but this absorption raises the temperature of the gases and increases the intensity of the radiant waves they send out. The effect of absorption of this reradiated heat by these gases is thus largely discounted.

The amount of heat received by furnace walls through direct radiation from the hot gases depends on the emissivities of those gases. For the purpose of studying these emissivities, these hot gases are classified under the following categories:

1. Inactive gases, including nitrogen, excess oxygen, carbon dioxide, and water vapor, which are not undergoing a chemical change and which contain no suspended solids, such as particles of carbon or of fly ash. Of these, the only important radiators are the carbon dioxide and the water vapor. Significant emissivities are also associated with unburned hydrocarbons, carbon monoxide, and sulfur dioxide, but the percentages of these gases are low.

2. Nonluminous flames, practically invisible in the furnace, which result from rapid combustion unaccompanied by cracking, or decomposition, of the fuel. The emissivity of nonluminous flames varies from about 0.1 to about 0.2.

3. Luminous flames, caused by the burning of small particles of solid carbon as they are carried in suspension. These carbon particles often result from the cracking of hydrocarbons in the course of their combustion. The emissivity is much higher than for the nonluminous flame, averaging around 0.7.

4. The gas mixture in the pulverized-coal furnace. This mixture includes not only particles of burning carbon but also unburned particles of solid fuel and particles of ash that have completed their combustion but are still held in suspension. This category has been given separate study because of its practical importance in the present-day power plant.

The subject of heat transmission by radiation from gases and flames is far too extended to be discussed in detail in these pages, and the reader is referred for more comprehensive treatment to other sources.<sup>1</sup>

**20:8. Effect of Convection on the Transmission of Heat by Conduction. Film Coefficients.** In our initial discussion of the effects of convection on the amount of heat transfer by conduction (see Art. 20:1), it has developed that those effects result from an increase in the temperature gradient of the fluid in the layers close to the surface of a solid wall; this change from the uniform temperature gradient to be expected in the fluid if there had been no convection has been pictured in Fig. 20:1. In the usual case the

<sup>1</sup> See Huber O. Croft, "Thermodynamics, Fluid Flow, and Heat Transmission," pp. 187-196, McGraw-Hill Book Company, Inc., New York, 1938; H. C. Hottel, *Trans. ASME*, 1935; Haslam and Hottel, *Trans. ASME*, 1928; Hottel and Mangelsdorf, *Trans. Am. Inst. Chem. Engrs.*, 1936.

temperatures of wall and fluid are low enough so that the heat flow by radiation between the two may be considered negligible; then it may be accepted that the heat transfer between wall surface and fluid is entirely by conduction. If the temperature gradient in the layers of fluid immediately adjacent to the wall surface is known, either Eq. (20:1) or Eq. (20:4) may be applied to the calculation of the heat flow. When Eq. (20:4) is used, it is written in the form

$$Q_{\text{cond}} = A \frac{k}{x} (t_2 - t_3)$$

in which  $x$  is the thickness of a layer of the fluid having one of its surfaces in immediate contact with the wall surface and which is thin enough so that the temperature gradient is constant. The temperature  $t_2$  is the common temperature of the wall surface and that surface of the fluid which is in contact with the wall;  $t_3$  is the temperature of the outer surface of the fluid layer. The constant temperature gradient through this thin film of fluid may then be substituted for  $(t_2 - t_3)/x$ .

This method of attack is of little use to the engineer, who usually begins his calculation of the amount of heat flow between two fluids with a knowledge of the fluid temperatures at points far enough removed from the wall separating the two so that the temperature gradient between these points and the wall surfaces with which the fluids are respectively in contact is not constant. The result of investigations into the effects of convection is therefore not reported in terms of the constant temperature gradient in the thin layer immediately adjacent to the wall but is expressed in terms of a *film coefficient*,  $h$ .<sup>\*</sup> This film coefficient replaces  $k/x$  in Eq. (20:4) and the temperature of the fluid ( $t_i$  or  $t_o$ ) replaces the intermediate (and unknown) temperature  $t_3$  which appeared when the temperature gradient was substituted. It will be observed [see Eq. (20:4)] that this film coefficient is equivalent to the conductance  $C$  of a layer of fluid of just sufficient thickness to span the temperature interval between the skin temperature of the wall and the plateau level of fluid temperature  $t_o$  (or  $t_i$ ). Through a layer of this thickness the temperature gradient is not constant, and the value of  $h$  must take account not only of the layer thickness (depending largely on the viscosity of the fluid and the velocity of its flow) and its conductivity  $k$  but also the average temperature gradient.

For some of the heat-transfer problems with which the engineer makes contact, the situation is more or less standardized, and it is feasible to determine the corresponding film coefficients by individual experiment and to publish them in tables for his use. For example, the film coefficient often used for an inside building surface is 1.6, for outside surfaces

<sup>\*</sup> Not to be confused with specific enthalpy, though represented by the same symbol. The film coefficient is sometimes called a *surface coefficient* of heat transfer.



6.0. In both these cases the fluid is air, the larger value of the second coefficient being principally based on the expectation that wind on the outside of a building will give a forced-circulation effect; the specific wind velocity associated with the value of 6.0 which is cited above is 15 mph. Values of film coefficients vary greatly, ranging upward to over 1000 Btu/(ft<sup>2</sup>)(°F)(hr) between wet steam and a cooler metal wall.

The selection of a suitable film coefficient from a table is usually possible when the problem deals with ordinary forms of building construction. Here conditions are largely standardized since the fluid on both sides of the wall is air, the range of temperature is not great, and the kind, shape, and size of the solid materials which form the intervening wall are limited in the number of their variations. For the heat exchanger of the engineering power plant, on the other hand, the factors are more varied, and resort is usually made to a different method of approach, to be discussed later. When the film coefficient has been determined, the heat flow per hour may be based on the variation of Eq. (20:4) below,

$$Q = hA(t_f - t_w) \quad (20:12)$$

in which  $t_f$  is the plateau level of fluid temperature at some distance from the wall and  $t_w$  is the skin temperature of that surface of the wall with which the fluid is in contact. Of these two temperatures,  $t_f$  is usually known to, or assumed by, the engineer as he enters upon the solution of the problem;  $t_w$  is unknown, and Eq. (20:12) alone is not sufficient for a solution. However, a wall such as is pictured in Fig. 20:2 has, if the laminations are composed of solid material, two film coefficients. Let us designate that at the left-hand surface as  $h_i$ , that at the right-hand surface as  $h_o$ . Since the heat flow through each lamination is the same and equal to the heat flow into the left-hand, and away from the right-hand, surface, we may write

$$h_i(t_i - t_1) = \frac{k_1}{x_1}(t_1 - t_2) = \frac{k_2}{x_2}(t_2 - t_3) = \frac{k_3}{x_3}(t_3 - t_4) = h_o(t_4 - t_o)$$

Four independent equalities are expressed above, and since the only unknowns are the four skin temperatures  $t_1, t_2, t_3, t_4$ , these temperatures may be established and the heat flow calculated.

**20:9. The Over-all Coefficient of Heat Transmission,  $U$ .** It has been noted that the film coefficient  $h$  is equivalent to the conductance of the fluid layers adjacent to the surface of the solid wall. The corresponding resistance of these fluid layers is therefore  $1/h$ . In Fig. 20:2, the resistance of the fluid films may be added to the resistance of the wall to give the over-all resistance to heat flow between the two plateau levels of fluid temperature,  $t_i$  and  $t_o$ . Thus

$$R_{\text{over-all}} = \frac{1}{h_i} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} + \frac{1}{h_o}$$

$$U = \frac{1}{R} = \frac{1}{\frac{1}{h_i} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} + \frac{1}{h_o}} \quad (20:13)$$

and

$$Q = AU(t_i - t_o) \quad (20:14)$$

in which  $U$  is the over-all conductance of the entire wall, including the effect of the resistance offered by the fluid films, and is called the *over-all heat-transfer coefficient*. When the situation is sufficiently standardized, values of  $U$  may be tabulated for various walls; these simplify the engineering calculation of the heat flow since the value of all terms on the right side of Eq. (20:14) are then usually readily and directly available to the engineer.

For reasons already explained, the practice of tabulating values of  $U$  for the engineer's use is commonest in the case of a building wall or other building surface. When one of the surfaces is an outside surface, it is customary to assume a wind velocity of 15 mph. Also, when a wall contains an interior air space, two additional inside-surface coefficients are often used in computing  $U$ . Tabulations of the values of  $U$  are also used in a few other engineering situations where heat-exchanger design has assumed some semblance of standardization. For example, the tubes of surface types of steam condensers are largely standardized as to size and material, the fluids are always the same, and the temperature variation is small; this makes it feasible to supply information to the engineer in the form of charts showing the value of  $U$  for condenser tubes according to their size and the velocity of water flow through them.

*Example 20:9A.* Assuming a wind velocity on the outside surface of 15 mph and using the film coefficients suggested in Art. 20:7, calculate the plateau temperatures  $t_i$  and  $t_o$  and the over-all heat-transmission coefficient  $U$  for (a) the wall of Example 20:4A and (b) the wall of Example 20:4B. (c) If the interior air space of the wall of Example 20:4B had not been filled with mineral wool, compute  $U$  by using two additional inside-surface coefficients. (d) What effect does the mineral wool have on the over-all conductivity of the wall?

*Solution:*

(a) From the solution of Example 20:4A,  $Q = 3940$  Btu/hr. Applying Eq. (20:12),

$$3940 = (1.6)(180)(t_i - 56.3) \text{ or } t_i = 70^\circ\text{F}$$

and

$$3940 = (6.0)(180)(3.7 - t_o) \text{ or } t_o = 0^\circ\text{F}$$

$$U = \frac{1}{\frac{1}{1.6} + \frac{12}{5} + \frac{1}{6}} = 0.313$$



Checking,

$$Q = AU(t_i - t_o) = (180)(0.313)(70 - 0) = 3940 \text{ Btu/hr}$$

(b) For the wall of Example 20:4B,

$$4.34 = (1.6)(1)(t_i - 67.3) \text{ or } t_i = 70^\circ\text{F}$$

$$4.34 = (6.0)(1)(0.7 - t_o) \text{ or } t_o = 0^\circ\text{F}$$

$$U = \frac{1}{\frac{1}{1.6} + \frac{1}{0.065} + \frac{1}{6}} = 0.062$$

Checking,

$$Q = (1)(0.062)(70 - 0) = 4.34 \text{ Btu/hr}$$

$$(c) U = \frac{1}{\frac{1}{1.6} + \frac{1}{2.5} + \frac{1}{1.6} + \frac{1}{1.6} + \frac{1.62}{0.80} + \frac{1}{6}} = 0.224$$

(d) The use of mineral wool reduces the over-all conductivity of the wall by

$$\left( \frac{0.224 - 0.062}{0.224} \right) (100) = 72 \text{ per cent}$$

*Example 20:9B.* In Example 20:4C, assume the inside coefficient is 1000 and the outside coefficient is 2 Btu/(ft<sup>2</sup>)(°F)(hr). (a) Assume that the pipe contains wet steam, and calculate its pressure. (b) What is the ambient temperature of the air surrounding the pipe? (c) What is the over-all heat-transfer coefficient of the pipe and insulation, based on area of inside surface?

*Solution:*

(a) The inside surface area, per foot of pipe length, is 1.05 ft<sup>2</sup>. Based on the solution of Example 20:4C,

$$81.2 = (1.05)(1000)(t_i - 300) \text{ and } t_i = 300.08^\circ\text{F}$$

For saturated steam, this temperature is equivalent to a pressure of 67.1 psia.

(b) The outside area of the insulation, per foot of pipe length, is  $8.5\pi/12 = 2.23 \text{ ft}^2$ .

$$81.2 = (2.23)(2)(90 - t_o) \text{ or } t_o = 71.8^\circ\text{F}$$

$$(c) U = \frac{Q}{A(t_i - t_o)} = \frac{81.2}{1.05(300.08 - 71.8)} = 0.339$$

**20:10. The Application of Dimensional Analysis.** Tables and charts giving the values of  $h$  or  $U$  may allow for only a limited number of variable factors. The total number of such factors that may play a part in heat transmission, when aided by convection, is large, as has been suggested in Art. 20:1. For the study of the less standard situation, dimensional analysis, to show the degree to which each of these factors enters, suggests itself.

Following the procedure of dimensional analysis (see Art. 17:3), we first decide upon the factors which are important in their influence on the

value of the film coefficient  $h$ . (Note that, dimensionally,  $[h] = [M/\theta^3 T]$ .) Let us suppose that these factors include:

$D$  = dimension of cross section of conduit through which fluid moves, as, for example, diameter of circular tube; dimensionally,  $[D] = [L]$

$\rho$  = mass density of fluid; dimensionally,  $[\rho] = \left[ \frac{M}{L^3} \right]$

$k$  = conductivity of fluid; dimensionally,  $[k] = \left[ \frac{ML}{\theta^3 T} \right]$

$\bar{V}$  = velocity of fluid; dimensionally,  $[\bar{V}] = \left[ \frac{L}{\theta} \right]$

$\mu$  = absolute viscosity of fluid; dimensionally,  $[\mu] = \left[ \frac{M}{L\theta} \right]$

$c_p$  = specific heat at constant pressure of fluid, dimensionally,  $[c_p] = \left[ \frac{L^2}{\theta^2 T} \right]$

$L$  = length of conduit; dimensionally,  $[L] = [L]$

The method of Art. 17:3 may now be followed to give

$$h = C \frac{k}{D} \left( \frac{\rho \bar{V} D}{\mu} \right)^a \left( \frac{c_p \mu}{k} \right)^b \left( \frac{D}{L} \right)^c$$

or

$$\frac{hD}{k} = C \left( \frac{\rho \bar{V} D}{\mu} \right)^a \left( \frac{c_p \mu}{k} \right)^b \left( \frac{D}{L} \right)^c \quad (20:15)$$

in which  $C$  is a dimensionless constant and  $a$ ,  $b$ , and  $c$  are exponents the values of which must be determined by experiment. The group  $hD/k$  is dimensionless and is known as the Nusselt number (Nu). The dimensionless group  $\rho \bar{V} D/\mu$  we recognize as the Reynolds number (Re). The group  $c_p \mu/k$ , also dimensionless, is called the Prandtl number (Pr).<sup>\*</sup> The value of the exponent  $c$  has been shown to be close to zero by experiment, and Eq. (20:15) is usually written in the form

$$\text{Nu} = C(\text{Re})^a(\text{Pr})^b \quad (20:16)$$

The values of  $h$ , of  $D$ , and of  $k$  must be in consistent units if the Nusselt number is to be dimensionless. Thus, for  $h$  in Btu/(ft<sup>2</sup>)(°F)(hr) and  $D$  in feet, the unit of  $k$  must be (Btu)(ft)/(ft<sup>2</sup>)(°F)(hr). The same consistency must be observed with regard to the units of the quantities of which the Reynolds and Prandtl numbers are composed. For the Prandtl number, the conventional unit of  $\mu$  is the lb-sec/ft<sup>2</sup> and of  $c_p$  the Btu/

<sup>\*</sup> Based on the varying selection of the important factors, other dimensionless numbers, *e.g.*, the Stanton, Peclet, and Grashof, also are found in the literature.



(lb mass)(°F). If, as in the Nusselt number, the unit of  $k$  is the (Btu)(ft)/(ft<sup>2</sup>)(°F)(hr), it is necessary, in making the time unit consistent, to multiply the conventional unit of viscosity by 3600 and, in making the mass units agree, to multiply the conventional unit of specific heat by  $g$ , or 32.2. Thus  $Pr = (3600)(32.2)(12)c_p\mu/k = 1,390,000c_p\mu/k$  with  $c_p$  and  $\mu$  in the conventional units suggested above and  $k$  in (Btu)(in.)/(ft<sup>2</sup>)(°F)(hr), the terms in which its values are tabulated in Table 20:1.

The Prandtl number is composed entirely of properties of the fluid and therefore is itself a property. For gases, and for vapors at pressures approximating atmospheric pressure, its value is close to 0.75. For vapors at relatively high pressure, its value is higher and tends to vary more widely with temperature. Liquids also show higher values of  $Pr$  and a larger variation with temperature; the variation with pressure is small.

That the effects of convection should vary with the Reynolds number is logical. We have seen in Chap. 17 that the Reynolds number not only establishes the point of transition from laminar to turbulent flow but also, in the higher range of values, is a key to the degree of turbulence. As the flow becomes more turbulent, the boundary layer becomes thinner and the temperature gradient in this layer greater, resulting in a higher rate of heat transfer.

The factors which have been selected earlier in this article and which have led, in dimensional analysis, to the development of Eq. (20:16) have been based on the assumption that the convection is forced, the velocity of fluid flow being primarily controlled by external agencies, such as pumps or fans, rather than being due solely to the differences in fluid density which are caused by temperature differences, as in natural convection. Under forced convection, the flow almost invariably lies in the turbulent range. The application of Eq. (20:16) is therefore primarily to forced-convection problems, and the values of  $Re$  which apply are usually relatively high. If natural convection is accompanied by a Reynolds number in the turbulent range, this relation may also be used.

The Nusselt equation (20:16) supplies a common pattern which can be followed by investigators of heat transmission in turbulent fluid flow in expressing the results of their experiments. When the fluid flows within a pipe round in cross section, as is often the case in the engineering problem, the problem is of a more standardized character and, as would be expected, closer agreement is found between results as reported by various experimenters. It is not within the scope of this text to list and compare the various equations that have been suggested. It will suffice for our purposes to say that, for turbulent flow inside a round pipe, the consensus seems to place the value of the exponent  $a$  in Eq. (20:16) at about 0.8, of  $b$  at 0.4, and of the exponent  $c$  in Eq. (20:15), when the  $D/L$  ratio is

included, at 0.05. There is less consistency in the values suggested for the dimensionless constant  $C$ , the recommended values falling in the approximate range 0.023 (when the ratio  $D/L$  is omitted) to 0.032 (with  $c = 0.05$ ).

The matter of whether the fluid is being heated or cooled will affect the amount of heat transfer and thus the size of the film coefficient, especially if the velocity of fluid flow is low. When the fluid receives heat, the layers of fluid adjacent to the solid wall from which the heat enters will be at higher temperature than the bulk of the fluid. If the fluid is a liquid, this higher temperature will mean that the fluid is less viscous near the wall and the parabolic velocity profile (see Chap. 17) is flattened, the ratio of average to maximum fluid velocity being increased. If a gas, increased temperature means increased viscosity and the layers of gas near the wall will be slowed, elongating the velocity profile and decreasing the ratio of average to maximum fluid velocity. Film-coefficient formulas often make an allowance for this effect by using different coefficients  $C$  for heating and for cooling. The difference is more pronounced for liquids than for gases, since the viscosity of liquids is more sensitive to temperature change. At the higher Reynolds numbers associated with forced convection, the effect is ordinarily negligible.

As the basis of the solution of exemplary problems, we shall select a comparatively simple relation to apply to the turbulent flow of fluids inside of round pipes,

$$\frac{hD}{k} = 0.023(\text{Re})^{0.8}(\text{Pr})^{0.4*} \quad (20:17)$$

in which the meaning of all terms has previously been discussed. Note that  $hD/k$  is the Nusselt number and the units of  $h$ ,  $D$ , and  $k$  must be selected so that it will be dimensionless. The equation is valid for Reynolds numbers above 3000; it may be applied to noncircular ducts with  $D$  equal to four times the hydraulic radius.

*Example 20:10A.* Air at atmospheric pressure and 120°F moves through a 10- by 16-in. rectangular steel duct with an average velocity of 20 fps. Calculate the inside film coefficient.

*Solution:*

$$\text{Hydraulic radius} = \frac{\text{cross-sectional area}}{\text{wetted perimeter}} = \frac{(10)(16)}{2(10 + 16)} = 3.07 \text{ in.}$$

$$D = 4 \left( \frac{3.07}{12} \right) = 1.02 \text{ ft}; \quad \frac{k}{12} = \left( \frac{0.163}{12} \right) [1 + (0.00165)(120 - 32)] = 0.0155$$

[Table 20:1]

$$c_p = 0.24 \text{ Btu}/(\text{lb mass})(^\circ\text{F})$$

$$\mu = [0.0165 + 2.5 \times 10^{-5}(120)]/47,800 = 4.07 \times 10^{-7} \text{ lb-sec}/\text{ft}^2 \quad [\text{Table 17:1}]$$

\* W. H. McAdams, "Heat Transmission," 2d ed., McGraw-Hill Book Company, Inc., 1942.



$$\rho = \frac{P}{gRT} = \frac{(14.7)(144)}{(32.2)(53.3)(580)} = 0.002125 \text{ slug/ft}^2$$

$$\text{Pr} = 1,390,000 \frac{c_p \mu}{k} = \frac{(1,390,000)(0.24)(4.07)(10^{-7})}{(12)(0.0155)} = 0.73; (\text{Pr})^{0.4} = 0.882$$

$$\text{Re} = \frac{\rho \bar{V} D}{\mu} = \frac{(0.002125)(20)(1.02 \times 10^7)}{4.07} = 106,000; (\text{Re})^{0.8} = 10,400$$

Substituting in Eq. (20:17),

$$\text{Nu} = \frac{12hD}{k} = (0.023)(0.882)(10,400) = 211$$

$$h = \frac{(211)(0.0155)}{1.02} = 3.2 \text{ Btu/ft}^2(\text{°F})(\text{hr})$$

The use of the value of 0.75 suggested in the text for Pr of gases will give  $(\text{Pr})^{0.4} = 0.891$  and change  $h$  in this problem to 3.24, a negligible difference.

When the fluid flows turbulently through an irregularly shaped conduit, as over the outside surfaces of a bank of tubes, the problem assumes a much less standardized pattern; for example, the selection of a representative dimension  $D$  is less readily made. Experiments usually are restricted to a narrower field of investigation, and results are sometimes reported in a form which is hardly recognizable as conforming to the basic equation (20:16). A complete survey is inappropriate to our discussion, and only one simple example will be given here of such equations. This is suggested by Still<sup>1</sup> and applies to the flow of gases normal to banks of tubes. For cooling of the gas, he gives

$$\text{Nu} = 0.279F(\text{Re})^{0.6} \quad (20:18)$$

and, for heating,

$$\text{Nu} = 0.29F(\text{Re})^{0.6} \quad (20:19)$$

In both of these equations  $F$  is a constant which depends on the number of rows of tubes in the direction of gas flow and their arrangement. If the rows are staggered,  $F$  varies from 1 for two rows of tubes to 1.335 for six rows; if the rows are in line, from 0.835 for two to 0.905 for six rows of tubes. It will be observed that the Prandtl number does not appear in these equations. However, if the fluid is a gas as specified, the Prandtl number has a nearly constant value which, raised to a suitable constant power, may be included in the constant. The dimension  $D$  in the Nusselt number refers to the outside diameter of the tubes, and  $k$  is based on the average temperature of the surface in using these equations. In the Reynolds number,  $\bar{V}$  is the gas velocity through the most constricted section, and both  $\rho$  and  $\mu$  are taken at the average temperature of the gas and the tube surface.

<sup>1</sup> *Proc. Inst. Mech. Engrs.*, **134** (1936).

*Example 20:10B.* In the back pass of a boiler, furnace gases at 600°F flow across a bank of six staggered rows of 3-in.-outside-diameter tubes with a maximum velocity of 8 fps. The surface temperature of the tubes averages 400°F. Calculate the outside film coefficient for these tubes.

*Solution:*

$$D = \frac{3}{12} = 0.25$$

The values for air will represent  $k$ ,  $\rho$ , and  $\mu$  for the hot gases.  $k$  is calculated at 400°F,  $\mu$  and  $\rho$  at  $(400 + 600)/2 = 500^\circ\text{F}$ .

$$\frac{k}{12} = \frac{0.163}{12} [1 + 0.00165(400 - 32)] = 0.0218$$

$$\mu = [0.0165 + (2.5 \times 10^{-5})(500)]/47,800 = 6.06 \times 10^{-7}$$

$$\rho = \frac{(14.7)(144)}{(32.2)(53.3)(960)} = 0.001285$$

$$\text{Re} = \frac{(0.001285)(8)(0.25)(10^7)}{6.06} = 4250; (\text{Re})^{0.6} = 150$$

For cooling of the gas, use Eq. (20:18); for six staggered rows of tubes,  $F = 1.335$ .

$$\text{Nu} = \frac{12hD}{k} = (0.279)(1.335)(150) = 55.8$$

$$h = \frac{(55.8)(0.0218)}{0.25} = 4.86 \text{ Btu}/(\text{ft}^2)(^\circ\text{F})(\text{hr})$$

**20:11. Calculation of Film Coefficients—Laminar Flow.** Under forced convection, laminar-flow conditions seldom exist. When they do, as sometimes in heat exchangers used in the refinement of viscous crude oils, Eq. (20:15) may be used as the basis for reporting the results of experiments; the value of the exponent  $a$  of the Reynolds number is usually reported as much smaller than the 0.8 of Eq. (20:17), which applies to turbulent flow.

But laminar flow usually is the result of natural convection. To attack the problem dimensionally requires that we add to the list of factors given in Art. 20:10, and which resulted in Eq. (20:16), additional factors which would assume importance in natural convection. These would include  $\Delta T$ , the difference between the temperature of the main body of the fluid (its plateau level of temperature) and the temperature of the wall surface;  $\beta$ , the coefficient of cubical expansion of the fluid, reflecting the effect of temperature changes on its density; and  $g$ , the acceleration of gravity. Other factors may, in special situations, be added to this list; for example, when the rate of change of viscosity with temperature is large, two viscosity factors may be introduced, the viscosity at the wall and the viscosity in the main body of the fluid.

For each additional factor that enters into the dimensional analysis, the number of dimensionless quantities appearing in the final result will be increased by one. Analysis or experiment may show the effect of many of these numbers to be slight, as was the case with the  $D/L$  ratio of Eq.



(20:15) in turbulent flow; as a result they may be dropped from the final relation so that its application may be simplified. In natural convection, the important dimensionless numbers are, in the general situation, the Prandtl number, previously discussed, and the Grashof number (Gr), defined as

$$\text{Gr} = \frac{\beta g \rho^2 \Delta T D^3}{\mu^2} \quad (20:20)$$

The meaning of all the terms has already been explained. Care must be observed to preserve the dimensionless character of the Grashof number in choosing the units of  $\beta$ ,  $g$ ,  $\rho$ ,  $\Delta T$ ,  $D$ , and  $\mu$ , but this is simpler than for the Prandtl number since the time period is the second in the conventional unit for all and the length unit is the foot. It will be observed that the Grashof number is not, like the Prandtl number, a property of the fluid but is rather to be compared with the Reynolds number.

When natural convection takes place on a vertical surface, or one inclined to the horizontal, whose vertical dimension is large, the dimensionless ratio  $D/L$  assumes greater relative importance. Assembling the important dimensionless numbers into an equation of the form of Eq. (20:16), but which will apply to natural convection, we have

$$\text{Nu} = C(\text{Pr})^b \left(\frac{D}{L}\right)^c (\text{Gr})^d \quad (20:21)$$

in which  $C$  is again a dimensionless constant and  $b$ ,  $c$ , and  $d$  are exponents. The values of all must be determined by experiment and may vary with the situation; for example, if the vertical dimension of the surface is small, the exponent  $c$  will approach zero in value, as it did for forced convection. As applied to horizontal cylinders (pipes), Nusselt determined the values of  $C = 0.99$ ,  $b = d = \frac{1}{4}$ , and  $c = 0$ . Thus, for horizontal pipes,

$$\text{Nu} = 0.99(\text{Pr})^{\frac{1}{4}}(\text{Gr})^{\frac{1}{4}} \quad (20:22)$$

For long vertical cylinders, Heilman<sup>1</sup> suggests that the coefficient  $C$  be changed to 1.2 to allow for the higher velocities created by the cumulative effect of convection on a vertical pipe. This increase in  $C$  takes the place of an inclusion of the ratio  $D/L$  in the equation. Thus, for long, vertical tubes,

$$\text{Nu} = 1.2(\text{Pr})^{\frac{1}{4}}(\text{Gr})^{\frac{1}{4}} \quad (20:23)$$

Equations (20:22) and (20:23) apply to the calculation of the film coefficient on either the outside or the inside surface of a tube and to both liquids and gases, provided only that the thickness of the film depends on

<sup>1</sup> *Trans. ASME, Fuels and Steam Power*, **51**(41), 297.

natural-convection effects. The values of  $k$ ,  $\rho$ ,  $\mu$ , and  $c_p$  used in computing the Prandtl and Grashof numbers are based on the mean temperature of the film.

*Example 20:11A.* A 4.5-in.-outside-diameter horizontal pipe carries warm water through a room in which the ambient temperature is 70°F. The temperature of the outside surface of the pipe is 210°F. Calculate the outside film coefficient of the pipe.

*Solution:*

$$D = 4.5/12 = 0.375; \Delta T = 210 - 70 = 140; g = 32.2$$

$\beta$ ,  $\rho$ , and  $\mu$  will be based on the average temperature of the film, or 140°F.  $k$  will be based on the surface temperature of the pipe, 210°F.  $\beta$  is the rate of change of air volume with temperature, which, at constant pressure, is  $1/T$ ; thus  $\beta = \frac{1}{600} = 0.00167$ .

$$\rho = \frac{(14.7)(144)}{(32.2)(53.3)(600)} = 0.00206$$

$$\mu = [0.0165 + (2.5 \times 10^{-5})(140)]/47,800 = 4.18 \times 10^{-7}$$

$$\text{Gr} = \frac{(0.00167)(32.2)(0.00206)^2(140)(0.375)^3(10)^{14}}{4.18^2} = 9,670,000; (\text{Gr})^{\frac{1}{4}} = 55.7$$

Assume  $\text{Pr} = 0.75$ . Then  $(\text{Pr})^{\frac{1}{4}} = 0.931$ .

$$\frac{k}{12} = \frac{0.163}{12} [1 + 0.00165(210 - 32)] = 0.0176$$

$$\text{Nu} = \frac{12hD}{k} = (0.99)(0.931)(55.7) = 51.3$$

$$h = \frac{(51.3)(0.0176)}{0.375} = 2.41 \text{ Btu}/(\text{ft}^2)(^\circ\text{F})(\text{hr})$$

A special situation of interest to the engineer is represented by the steam condenser, so frequently a part of the equipment of the steam power plant. In the surface type of steam condenser, an essentially quiet body of exhaust steam surrounds banks of tubes, usually horizontal, through which cooling water is forced. The film coefficient on the outside of these tubes is based on natural convection but is affected by the film of condensate which forms on the tube surface and through which the heat must pass. Occasionally, when the tubes are new and the outside surface is polished, or when coated with a thin film of oil, the condensation may form as droplets. Drop condensation produces much larger film coefficients, but since the surface of the tube soon becomes oxidized in use and this is favorable to the formation of a film, it is usually assumed for the purposes of design that film condensation applies. Nusselt<sup>1</sup> derived an equation to apply to film condensation, as follows:

$$h = 5.62 \left( \frac{k^3 \rho^2 g^2 h_{fg}}{D \mu \Delta T} \right)^{\frac{1}{4}} \quad (20:24)$$

<sup>1</sup> Z. Ver. Deut. Ing., **60**, 541, 569 (1916).



in which  $h$  = film coefficient, Btu/(ft<sup>2</sup>)(°F)(hr)

$k$  = conductivity of liquid condensate, (Btu)(ft)/(ft<sup>2</sup>)(°F)(hr)

$\rho$  = mass density of condensate, slugs/(ft<sup>3</sup>)

$g$  = acceleration of gravity, ft/sec<sup>2</sup>

$h_{fg}$  = enthalpy of vaporization of vapor, Btu/lb

$D$  = diameter of tube, ft

$\mu$  = absolute viscosity of the condensate, lb-sec/ft<sup>2</sup>

$\Delta T$  = temperature difference between vapor and the tube surface, °F

It will be observed that the product  $\rho g$  is the weight density in pounds per cubic foot and that the square of the weight density of the liquid may therefore be substituted for  $\rho^2 g^2$  in the equation. The temperature at which  $k$ ,  $\rho$ , and  $\mu$  are calculated is the average of the temperatures of the wall and the steam;  $h_{fg}$  at steam temperature is used. The value of  $h$  obtained is large, usually above 1000, and the equation is often by-passed in favor of the use of an assumed value of 1000; this practice is considered conservative in steam-condenser design. Even when  $h$  is as high as 2000, a relatively small effect will be produced on  $U$ , the over-all heat-transmission coefficient of the tube, by using the smaller value.

*Example 20-11B.* The water vapor in a condenser has a temperature of 100°F. The condenser tubes are 1 in. outside diameter and have an average outside-surface temperature of 80°F. Calculate the average outside film coefficient for these tubes.

*Solution:*

$D = \frac{1}{12} = 0.0833$ ;  $h_{fg}$  (at 100°F) = 1037.2.  $k$ ,  $\rho$ , and  $\mu$  are calculated for water at the average between steam and surface temperature, or 90°F.

$$\frac{k}{12} = \left( \frac{4.1}{12} \right) [1 + 0.001(90 - 68)] = 0.35$$

$$\rho g = \frac{1}{0.01610} = 62.1 \text{ lb/ft}^3$$

$$\mu = [2.317 - (0.0164)(90)]/47,800 = 1.75 \times 10^{-5}$$

$$h = 5.62 \left[ \frac{(0.35)^3 (62.1)^2 (1037.2)(10^5)}{(0.0833)(1.75)(20)} \right]^{\frac{1}{4}} = 5.62(59 \times 10^8)^{\frac{1}{4}} \\ = 1560 \text{ Btu/(ft}^2\text{)(°F)(hr)}$$

**20:12. Mean Temperature Difference.** When the temperature of one, or both, of the fluids that exchange heat as they pass through the heat exchanger changes between entrance to and exit from that unit, a knowledge of the mean, or average, temperature difference between these fluids is necessary if equations such as (20:14) are to be applied to the calculation of the heat given up by the one and received by the other in the course of their entire flows through the unit. This mean temperature difference can then be substituted for  $t_i - t_o$  in Eq. (20:14). One of the simplest examples is supplied by the steam condenser, where one of the fluids remains at constant temperature while the other increases in temperature

from inlet to outlet; it is illustrated in Fig. 20:7. The area of the solid wall which separates the fluids is represented along the abscissa of this figure, and it is assumed that each

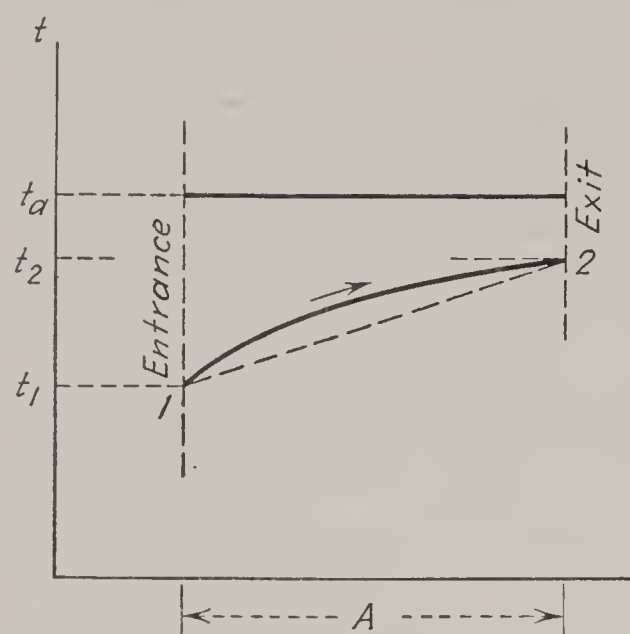


FIG. 20:7. Mean temperature difference—condensation of a vapor.

unit area of this wall has the same over-all heat-transmission coefficient  $U$ ; it is also assumed that heat leaving the hot fluid exactly equals that entering the cold. The constant temperature of the warmer fluid is designated as  $t_a$ , the entering temperature of the cooler as  $t_1$ , and its exit temperature as  $t_2$ . The direction of flow of the cooler fluid is indicated by the arrow.

The temperature difference  $t_a - t_1$  is greater near the entrance to the heat exchanger than at the exit, where it is  $t_a - t_2$ . The cold fluid therefore receives heat at a more rapid rate per unit of wall area near the entrance and will increase in temperature more rapidly than as the exit is approached; the solid curve 1-2 will approximate the temperature variation with surface area traversed.

There are two more general cases, for each of which the temperature of the hot fluid does not remain constant but decreases from  $t_a$  to  $t_b$  as it gives up heat. The first of these is illustrated in Fig. 20:8 and represents the temperature variation of the fluids as they pass through a *parallel-flow* heat exchanger. The two fluids enter at the same end of the heat exchanger and approach each other in temperature as they flow through it; the final temperature of the cold fluid is always less than the temperature at which the hot fluid leaves the exchanger. The difference between the temperatures of the two fluids at entrance is always greater than at exit, and the temperature variation is shown by the two curves,  $ab$  and 1-2, which bend toward each other.

In approaching the problem of calculating the mean temperature difference between the fluids for the entire heat exchange, let us consider a sec-

figure, and it is assumed that each unit area of this wall has the same over-all heat-transmission coefficient  $U$ ; it is also assumed that heat leaving the hot fluid exactly equals that entering the cold. The constant temperature of the warmer fluid is designated as  $t_a$ , the entering temperature of the cooler as  $t_1$ , and its exit temperature as  $t_2$ . The direction of flow of the cooler fluid is indicated by the arrow.

The temperature difference  $t_a - t_1$  is greater near the entrance to the heat exchanger than at the exit, where

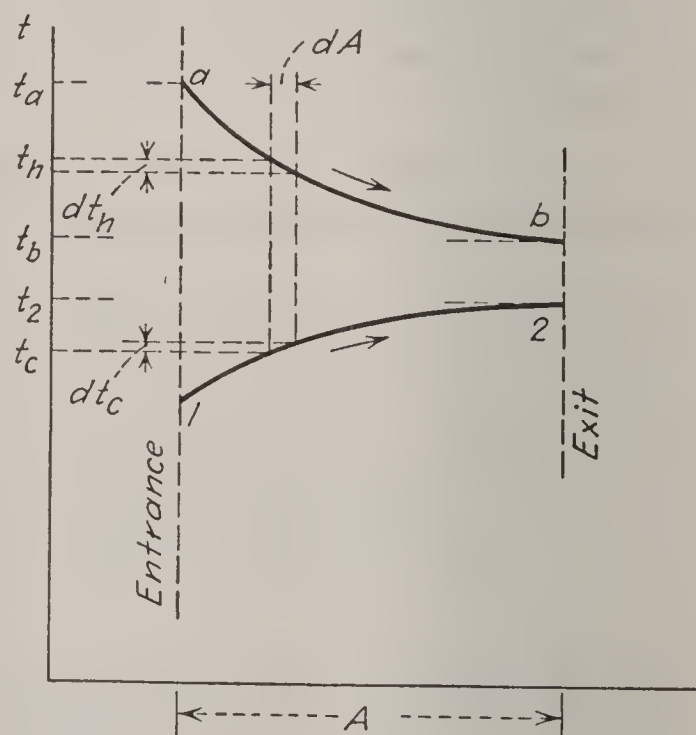


FIG. 20:8. Variation of fluid temperature—parallel-flow heat exchanger.



tion of the heater having a surface of the elementary area  $dA$ . The hot fluid enters this section of the heater at a rate which we shall designate as  $M_h$  lb/hr and a temperature of  $t_h$ ; its temperature is  $t_h + dt_h$  (where  $dt_h$  is negative) as it leaves the heater section. Designating the specific heat of the hot fluid as  $c_h$ , we may write

$$\partial Q_h = M_h c_h dt_h \quad (1)$$

in which  $\partial Q_h$  is the heat leaving the hot fluid as it passes over the elementary surface area  $dA$ ; it is negative in sign according to the convention we have adopted. Similarly, for the cold fluid,

$$\partial Q_c = M_c c_c dt_c \quad (2)$$

in which the meaning of all terms is the same as in (1) but the subscript  $c$  refers to the cold fluid; since  $\Delta t_c$  is positive,  $\partial Q_c$  must be positive.  $\partial Q_h$  and  $\partial Q_c$  are equal but opposite in sign, and therefore

$$\partial Q_h = M_h c_h dt_h = -M_c c_c dt_c \quad (3)$$

or

$$dt_h = \partial Q_h \left( \frac{1}{M_h c_h} \right) \quad \text{and} \quad -dt_c = \partial Q_h \left( \frac{1}{M_c c_c} \right) \quad (4)$$

The difference,  $dt_h - dt_c$ , is the amount by which the difference between the temperatures of the two fluids changes, or

$$dt_h - dt_c = d(t_h - t_c) = \partial Q_h \left( \frac{1}{M_h c_h} + \frac{1}{M_c c_c} \right) \quad (5)$$

The difference in temperature  $t_h - t_c$  controls the rate of heat flow between the two fluids through the surface area  $dA$ . According to Eq. (20:14),

$$\partial Q_h = -U(t_h - t_c) dA \quad (6)$$

Substituting this value of  $\partial Q_h$  in (5) and rearranging,

$$\frac{d(t_h - t_c)}{t_h - t_c} = -U \left( \frac{1}{M_h c_h} + \frac{1}{M_c c_c} \right) dA \quad (7)$$

The left side of this equation will be integrated between the limits set by the temperature difference  $t_a - t_1$  at entrance, which will be designated as  $\Delta t'$ , and that at exit,  $t_b - t_2$ , designated as  $\Delta t''$ . The limits for the integration of the right side are 0 and  $A$ . Then

$$\int_{\Delta t'}^{\Delta t''} \frac{d(t_h - t_c)}{t_h - t_c} = -U \left( \frac{1}{M_h c_h} + \frac{1}{M_c c_c} \right) \int_0^A dA \quad (8)$$

or

$$\log_e \frac{\Delta t''}{\Delta t'} = -UA \left( \frac{1}{M_h c_h} + \frac{1}{M_c c_c} \right) \quad (9)$$

But

$$Q_h = -UA (\Delta t)_m$$

or

$$-UA = \frac{Q_h}{(\Delta t)_m} = \frac{M_h c_h (t_b - t_a)}{(\Delta t)_m} = \frac{M_c c_c (t_1 - t_2)}{(\Delta t)_m} \quad (10)$$

in which  $(\Delta t)_m$  is the mean temperature difference through the entire heat exchange. Substituting this value of  $-UA$  in (9), we obtain

$$\log_e \frac{\Delta t''}{\Delta t'} = \frac{t_b - t_a + t_1 - t_2}{(\Delta t)_m} = \frac{\Delta t'' - \Delta t'}{(\Delta t)_m} \quad (11)$$

or

$$(\Delta t)_m = \frac{\Delta t'' - \Delta t'}{\log_e (\Delta t''/\Delta t')} \quad (12)$$

It will be noted that the positions of  $\Delta t'$  and  $\Delta t''$  may be interchanged in this equation without affecting the value of  $(\Delta t)_m$ .  $(\Delta t)_m$  is called the *logarithmic mean temperature difference* (LMTD) and therefore

$$\text{LMTD} = \frac{\Delta t'' - \Delta t'}{\log_e (\Delta t''/\Delta t')} \quad (20:25)$$

in which  $\Delta t''$  is the temperature difference between the fluids at either end of the heat exchanger,  $\Delta t'$  being the difference at the other end.

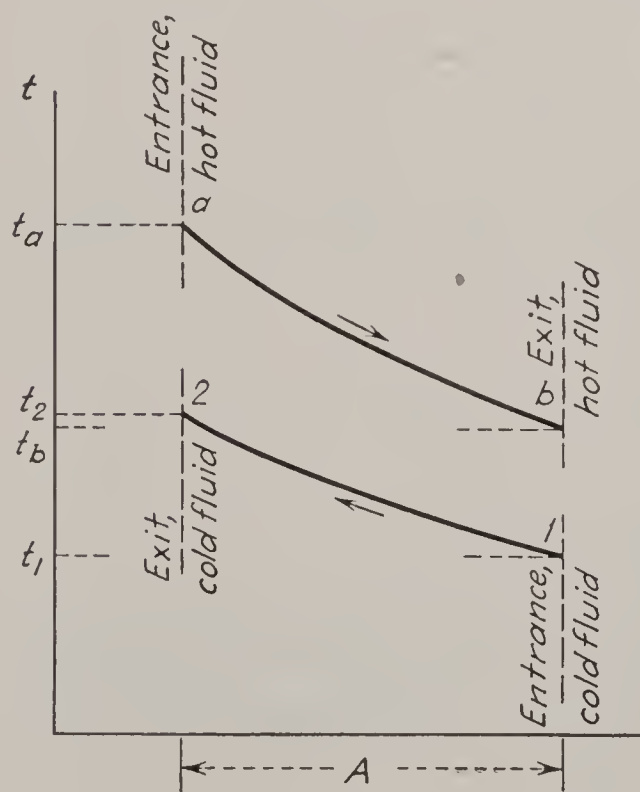


FIG. 20:9. Variation of fluid temperature—counterflow heat exchanger.

Figure 20:9 illustrates the *counter-flow* principle in heat-exchanger design in which the fluids enter at opposite ends of the heat exchanger and flow in opposite directions through the unit. Note that, in counterflow, the final temperature of the cold fluid may exceed the final temperature of the fluid which gives up heat and a lower average temperature difference is possible. It may be shown that Eq. (20:25) will apply as well to the calculation of the mean temperature difference for this situation (and to the conditions illustrated in Fig. 20:7) as for the parallel flow on which its derivation was based. If  $M_h c_h = M_c c_c$  in counterflow, the temperature difference between the fluids will remain constant. Equation (20:25) gives an indeterminate value for this special condition, but the *arithmetical mean temperature difference* (AMTD) may be used. This is a simple

ence between the fluids will remain constant. Equation (20:25) gives an indeterminate value for this special condition, but the *arithmetical mean temperature difference* (AMTD) may be used. This is a simple



arithmetical average between  $\Delta t'$  and  $\Delta t''$ . For the cases illustrated in Figs. 20:7 and 20:8, Eq. (20:25) should always be used, for the AMTD assumes that the temperature of the fluid follows a straight line between its initial and final values (see the dashed line 1-2 of Fig. 20:7); the calculation of the AMTD will therefore show a value higher than the true mean temperature difference. In counterflow design,  $\Delta t'$  and  $\Delta t''$ , even when not equal, may be so nearly the same that difficulty will be experienced in evaluating LMTD by Eq. (20:25). In that case, it may be better to use the AMTD. When  $\Delta t'$  and  $\Delta t''$  are equal, the LMTD and the AMTD are, of course, identical values; this may occur not only in counterflow but also when heat is exchanged between fluids one of which is condensing, the other evaporating, at respectively constant temperatures. The counterflow principle makes it possible, in theory, to design a heat exchanger to operate on an infinitesimal temperature difference and thus avoid irreversibility in heat exchange.

### Problems

1. A sheet of steel 10 by 12 ft,  $\frac{1}{16}$  in. in thickness, separates two flowing gas streams which differ in temperature. The surface temperatures of the steel wall differ by  $2^\circ\text{F}$ . How much heat flows through the wall per minute?

2. A *stationary* layer of air fills the space between two parallel steel walls which are 2 ft apart. If the interior-surface temperatures of the steel walls are  $300$  and  $100^\circ\text{F}$ , respectively, calculate the rate of heat transfer per hour per square foot of area of each wall. Repeat, changing the surface temperatures to  $400$  and  $200^\circ\text{F}$ . Neglect radiation.

3. A layer of corkboard with an area of  $10\text{ ft}^2$  allows the flow of 90 Btu of heat per hour when its surface temperatures are  $80$  and  $20^\circ\text{F}$ . What is its thickness? What is its conductance? Its resistance?

4. A wall has a thickness of 8 in. and an area of  $100\text{ ft}^2$ . When the surface temperatures are  $150$  and  $70^\circ\text{F}$ , the heat transfer is 6500 Btu/hr. What is the conductivity of the wall? What is its conductance? Its resistance?

5. A test specimen of brick building wall 8 in. thick allows the transfer of 200 Btu during a 30-min test. A temperature differential of  $90^\circ\text{F}$  is maintained between the two wall surfaces. What is the area of the wall?

6. A brick-veneer building wall consists of a 4-in. thickness of brick, pine sheathing  $\frac{1}{8}$  in. thick, a  $3\frac{1}{2}$ -in. space which is filled with mineral wool, and an inner layer of wood lath and plaster,  $\frac{3}{4}$  in. in thickness. Calculate (a) the conductance of this wall and (b) the temperature at the inner surface of the brick when its outer-surface temperature is  $5^\circ\text{F}$  and the temperature of the exposed surface of the plaster is  $60^\circ\text{F}$ .

7. A furnace wall consists of a 9-in. thickness of refractory (fire-clay) brick, a 3-in. thickness of insulation [ $k = 0.5\text{ (Btu)(in.)/(ft}^2\text{)(}^\circ\text{F)(hr)}$ ], and 4 in. of common brick. The inside-surface temperature of this wall (the refractory-brick surface) is  $1400^\circ\text{F}$ , and its outside- (common-brick) surface temperature is  $110^\circ\text{F}$ . Calculate (a) the conductance of the wall and (b) the average temperature of the layer of refractory brick.

8. A steel boiler tube is  $3\frac{1}{2}$  in. outside diameter, 0.12 in. thick. Its inside-surface temperature is  $400^\circ\text{F}$ . If heat is transferred to the water inside the tube at a rate of 4000 Btu/hr per foot of pipe length, what is the temperature of the outside surface?

9. In Prob. 8 assume that boiler scale ( $k = 15$ ) has accumulated to a thickness of  $\frac{1}{16}$  in. on the inside of the pipe. The temperature of the inner surface of this scale is  $400^\circ\text{F}$ . Assuming the rate of heat transfer is the same as in Prob. 8, calculate the temperature of the outside surface of the pipe.

10. In Example 20:4C, assume that the inner surface of the pipe is coated with a layer of boiler scale  $\frac{1}{16}$  in. in thickness ( $k = 15$ ). The surface temperatures are as in the example, except that the surface temperature of  $300^\circ\text{F}$  applies to the inner surface of the scale. Calculate (a) the percentage reduction in heat transfer and (b) the surface temperatures of the steel pipe.

11. A  $3\frac{1}{2}$  in.-outside-diameter steel tube, 10 ft long, carries steam through a passage 30 in. in diameter and lined with white firebrick. The outside-surface temperature of the pipe is  $300^\circ\text{F}$ ; the inside-surface temperature of the firebrick is  $1000^\circ\text{F}$ . Calculate the radiant heat absorbed per hour by the pipe if (a) the pipe is considered to be completely enclosed and (b) if the two surfaces are treated as concentric infinite cylinders.

12. A 4-in.-outside-diameter bare steel pipe, 20 ft long, carries steam through a room the plastered walls of which have a surface temperature of  $100^\circ\text{F}$ . The surface temperature of the pipe is  $400^\circ\text{F}$ . (a) Calculate the heat loss per hour from the pipe by radiation. (b) By covering the pipe with a 1-in. layer of asbestos insulation, its surface temperature may be reduced to  $140^\circ\text{F}$ . What is the percentage reduction in the heat loss by radiation as compared with part a?

13. A horizontal bank of water tubes is located 20 ft above and parallel with a 16- by 22-ft furnace floor. The tubes are staggered so that all radiant heat is intercepted. The side walls of the furnace may reradiate but are assumed to absorb none of the radiant heat from the floor, which is constructed of light buff refractory brick and has a surface temperature of  $2000^\circ\text{F}$ . The surface temperature of the tubes is  $400^\circ\text{F}$ . Calculate the radiant heat received per hour by the tubes.

14. In Example 20:6A, change the dimensions of the furnace to 18 by 24 ft, with a height of 18 ft. The tube bank covers one of the 24-ft vertical walls. Assume the tube surface temperature to be  $400^\circ\text{F}$  and the surface temperature of the walls to be  $2000^\circ\text{F}$ . Calculate the radiant heat received by the tube bank (a) from each of the adjacent vertical walls and (b) from the opposite vertical wall.

15. In Prob. 1, assume both surface coefficients to be 1.5. What is the total difference between the free-stream temperatures of the two gas flows?

16. In Prob. 2, if the layer of air is not stationary but has a surface coefficient of 2 at both walls, find the temperature at the center of the layer and the rate of heat transfer per hour per square foot of wall area. Assume wall-surface temperatures of 100 and  $300^\circ\text{F}$ , and compare your answer with the answer to Prob. 2.

17. What temperature gradient in the layers of air immediately adjacent to the wall surface corresponds (a) to the surface coefficient of 1.6 suggested for inside walls in Art. 20:8? (b) To the outside surface coefficient of 6.0?

18. (a) Calculate the over-all heat-transfer coefficient for the wall described in Prob. 6. Assume an outside wind velocity of 15 mph. (b) If the  $3\frac{1}{2}$ -in. space had not been filled with mineral wool, what would have been the over-all heat-transfer coefficient for the wall?

19. In Prob. 7, assume that the inside-surface coefficient is 4, the outside is 1.6. What are the plateau levels of temperature of the hot gases inside and the air outside the wall?

20. Show in detail the steps in the derivation of Eq. (20:15).

21. Calculate the Prandtl number for air at atmospheric pressure and (a) a temperature of  $50^\circ\text{F}$ ; (b) a temperature of  $200^\circ\text{F}$ . Do the same for hydrogen, and compare. For saturated steam at  $212^\circ\text{F}$ .



22. Calculate the Prandtl number for liquid water at (a) 50°F; (b) at 200°F.
23. Calculate the average inside film coefficient when 600 ft<sup>3</sup> of air per minute at atmospheric pressure and an average temperature of 140°F is carried by a rectangular 8- by 12-in. duct.
24. SAE 30 lubricating oil (specific gravity = 0.88;  $c_p$  = 0.50) is forced through a pipe with an internal diameter of 2.07 in. at an average velocity of 10 fps. The average pressure of the oil is 40 psia, and its average temperature is 150°F. Determine the average inside film coefficient.
25. A 1-in. pipe (internal diameter = 1.05 in.) discharges 30 gal of water per minute at 180°F. Determine the inside film coefficient at a point in the pipe where the pressure is 70 psia, the temperature 200°F.
26. Superheated steam at 500 psia, 600°F (see steam tables for its viscosity and conductivity), moves through a pipe with an internal diameter of 5.85 in. at a velocity of 100 fps. Find the inside film coefficient.
27. A stream of air is heated in passing through a bank of four staggered rows of 1-in. steam pipe (1.3 in. outside diameter) in a direction normal to the plane of the bank. The outside-surface temperature of the tubes averages 210°F, and the average temperature of the air is 80°F. The velocity of air flow is 10 fps in the most constricted section. Calculate the average outside film coefficient. Assume a straight-line variation of  $F$  with the number of rows of tubes.
28. In Example 20:4C, assume that the pipe is horizontal and passes through a room with an ambient-air temperature of 70°F. The temperature at the outer surface of the insulation is 90°F. (a) Calculate the outside film coefficient of the pipe. (b) Based on your answer to part a, calculate the rate of heat flow from the outer surface of the pipe per foot of pipe length. Compare with the rate of heat transfer through the pipe and insulation, as calculated in the example, and decide whether the surface temperature of the insulation is above or below 90°F when the ambient-air temperature is 70°F. Determine the surface temperature of the pipe for a proper balance of heat flows.
29. Repeat Prob. 28, but assume the pipe to be vertical.
30. The condenser tubes of Example 20:11B are made of copper and have a wall thickness of 0.08 in. Assume that the water temperature is negligibly lower than the outside-surface temperature of the tubes (80°F) and that the average cooling-water velocity is 10 fps. (a) Calculate the inside film coefficient. (b) Using the outside film coefficient as calculated in the example, compute the over-all coefficient of heat transmission (steam to water). (c) Calculate the over-all coefficient of heat transmission as based on an outside film coefficient of 1000, and compare with the answer to part b.
31. Steam is condensed at a pressure of 1 in. Hg abs in a surface condenser. The tubes are  $\frac{7}{8}$  in. outside diameter, and their average outside-surface temperature is 60°F. Calculate the average outside film coefficient.
32. If the LMTD between steam and cooling-water temperatures in a surface condenser is 20°F, the temperature of the steam is 100°F, and the water enters at 75°F, calculate the temperature of the water at exit from the condenser.
33. In an air preheater, the counterflow principle is employed, and the air enters at 70°F and is heated to 250°F. The flue gas enters at 600°F, and its mass rate of flow is 10 per cent greater than that of the air. The specific heats of the air and of the flue gas may be assumed equal. Calculate the LMTD.

### Symbols

- $a$  absorptivity (=  $\epsilon$ )  
 $A$  area

$c$	specific heat
$c_p$	specific heat at constant pressure
$C_1$	a constant
$C$	thermal conductance; also, a dimensionless coefficient
$D$	a dimension; for round pipes, the diameter
$F_c$	configuration factor
$F_e$	emissivity factor
$g$	acceleration of gravity
$h$	film, or surface, coefficient in convective heat transfer
$k$	thermal conductivity; conductance of a homogeneous wall of unit thickness
$L$	the dimension of length; also, length
$M$	the dimension of mass; also, mass rate of flow
Nu	Nusselt number ( $hD/k$ )
$P$	pressure
Pr	Prandtl number ( $c_p\mu/k$ )
$Q$	rate of heat flow
$r$	radius
$R$	thermal resistance ( $= 1/C$ )
Re	Reynolds number
$t$	scalar temperature
$T$	the dimension of temperature; also, absolute temperature
$U$	over-all heat transfer coefficient
$\bar{V}$	velocity
$x$	thickness

*Greek Letters*

$\beta$	coefficient of cubical expansion
$\epsilon$	emissivity
$\theta$	the dimension of time
$\mu$	viscosity
$\rho$	mass density
$\sigma$	Stefan's constant

*Subscripts*

$c$	cold fluid
cond	conducted; by conduction
$f$	fluid
$h$	hot fluid
$i$	inside
$m$	mean, or average
$o$	outside
$p$	constant pressure
rad	radiated; by radiation
$w$	wall surface
0	reference, or base, level of temperature



## APPENDIX

TABLE 1  
DRY SATURATED STEAM: TEMPERATURE TABLE \*

Temp., F <i>t</i>	Abs Press., Lb Sq In. <i>p</i>	Specific Volume			Enthalpy			Entropy			Temp., F <i>t</i>
		Sat. Liquid <i>v<sub>f</sub></i>	Evap. <i>v<sub>fg</sub></i>	Sat. Vapor <i>v<sub>g</sub></i>	Sat. Liquid <i>h<sub>f</sub></i>	Evap. <i>h<sub>fg</sub></i>	Sat. Vapor <i>h<sub>g</sub></i>	Sat. Liquid <i>s<sub>f</sub></i>	Evap <i>s<sub>fg</sub></i>	Sat. Vapor <i>s<sub>g</sub></i>	
32	0.08854	0.01602	3306	3306	0.00	1075.8	1075.8	0.0000	2.1877	2.1877	32
35	0.09995	0.01602	2947	2947	3.02	1074.1	1077.1	0.0061	2.1709	2.1770	35
40	0.12170	0.01602	2444	2444	8.05	1071.3	1079.3	0.0162	2.1435	2.1597	40
45	0.14752	0.01602	2036.4	2036.4	13.06	1068.4	1081.5	0.0262	2.1167	2.1429	45
50	0.17811	0.01603	1703.2	1703.2	18.07	1065.6	1083.7	0.0361	2.0903	2.1264	50
60	0.2563	0.01604	1206.6	1206.7	28.06	1059.9	1088.0	0.0555	2.0393	2.0948	60
70	0.3631	0.01606	867.8	867.9	38.04	1054.3	1092.3	0.0745	1.9902	2.0647	70
80	0.5069	0.01608	633.1	633.1	48.02	1048.6	1096.6	0.0932	1.9428	2.0360	80
90	0.6982	0.01610	468.0	468.0	57.99	1042.9	1100.9	0.1115	1.8972	2.0087	90
100	0.9492	0.01613	350.3	350.4	67.97	1037.2	1105.2	0.1295	1.8531	1.9826	100
110	1.2748	0.01617	265.3	265.4	77.94	1031.6	1109.5	0.1471	1.8106	1.9577	110
120	1.6924	0.01620	203.25	203.27	87.92	1025.8	1113.7	0.1645	1.7694	1.9339	120
130	2.2225	0.01625	157.32	157.34	97.90	1020.0	1117.9	0.1816	1.7296	1.9112	130
140	2.8886	0.01629	122.99	123.01	107.89	1014.1	1122.0	0.1984	1.6910	1.8894	140
150	3.718	0.01634	97.06	97.07	117.89	1008.2	1126.1	0.2149	1.6537	1.8685	150
160	4.741	0.01639	77.27	77.29	127.89	1002.3	1130.2	0.2311	1.6174	1.8485	160
170	5.992	0.01645	62.04	62.06	137.90	996.3	1134.2	0.2472	1.5822	1.8293	170
180	7.510	0.01651	50.21	50.23	147.92	990.2	1138.1	0.2630	1.5480	1.8109	180
190	9.339	0.01657	40.94	40.96	157.95	984.1	1142.0	0.2785	1.5147	1.7932	190
200	11.526	0.01663	33.62	33.64	167.99	977.9	1145.9	0.2938	1.4824	1.7762	200
210	14.123	0.01670	27.80	27.82	178.05	971.6	1149.7	0.3090	1.4508	1.7598	210
212	14.696	0.01672	26.78	26.80	180.07	970.3	1150.4	0.3120	1.4446	1.7566	212
220	17.186	0.01677	23.13	23.15	188.13	965.2	1153.4	0.3239	1.4201	1.7440	220
230	20.780	0.01684	19.365	19.382	198.23	958.8	1157.0	0.3387	1.3901	1.7288	230
240	24.969	0.01692	16.306	16.323	208.34	952.2	1160.5	0.3531	1.3609	1.7140	240
250	29.825	0.01700	13.804	13.821	218.48	945.5	1164.0	0.3675	1.3323	1.6998	250
260	35.429	0.01709	11.746	11.763	228.64	938.7	1167.3	0.3817	1.3043	1.6860	260
270	41.858	0.01717	10.044	10.061	238.84	931.8	1170.6	0.3958	1.2769	1.6727	270
280	49.203	0.01726	8.628	8.645	249.06	924.7	1173.8	0.4096	1.2501	1.6597	280
290	57.556	0.01735	7.444	7.461	259.31	917.5	1176.8	0.4234	1.2238	1.6472	290



300	67.013	0.01745	6.449	6.466	269.59	910.1	1179.7	0.4369	1.1980	1.6350	300
310	77.68	0.01755	5.609	5.626	279.92	902.6	1182.5	0.4504	1.1727	1.6231	310
320	89.66	0.01765	4.896	4.914	290.28	894.9	1185.2	0.4637	1.1478	1.6115	320
330	103.06	0.01776	4.289	4.307	300.68	887.0	1187.7	0.4769	1.1233	1.6002	330
340	118.01	0.01787	3.770	3.788	311.13	879.0	1190.1	0.4900	1.0992	1.5891	340
350	134.63	0.01799	3.324	3.342	321.63	870.7	1192.3	0.5029	1.0754	1.5783	350
360	153.04	0.01811	2.939	2.957	332.18	862.2	1194.4	0.5158	1.0519	1.5677	360
370	173.37	0.01823	2.606	2.625	342.79	853.5	1196.3	0.5286	1.0287	1.5573	370
380	195.77	0.01836	2.317	2.335	353.45	844.6	1198.1	0.5413	1.0059	1.5471	380
390	220.37	0.01850	2.0651	2.0836	364.17	835.4	1199.6	0.5539	0.9832	1.5371	390
400	247.31	0.01864	1.8447	1.8633	374.97	826.0	1201.0	0.5664	0.9608	1.5272	400
410	276.75	0.01878	1.6512	1.6700	385.83	816.3	1202.1	0.5788	0.9386	1.5174	410
420	308.83	0.01894	1.4811	1.5000	396.77	806.3	1203.1	0.5912	0.9166	1.5078	420
430	343.72	0.01910	1.3308	1.3499	407.79	796.0	1203.8	0.6035	0.8947	1.4982	430
440	381.59	0.01926	1.1979	1.2171	418.90	785.4	1204.3	0.6158	0.8730	1.4887	440
450	422.6	0.0194	1.0799	1.0993	430.1	774.5	1204.6	0.6280	0.8513	1.4793	450
460	466.9	0.0196	0.9748	0.9944	441.4	763.2	1204.6	0.6402	0.8298	1.4700	460
470	514.7	0.0198	0.8811	0.9009	452.8	751.5	1204.3	0.6523	0.8083	1.4606	470
480	566.1	0.0200	0.7972	0.8172	464.4	739.4	1203.7	0.6645	0.7868	1.4513	480
490	621.4	0.0202	0.7221	0.7423	476.0	726.8	1202.8	0.6766	0.7653	1.4419	490
500	680.8	0.0204	0.6545	0.6749	487.8	713.9	1201.7	0.6887	0.7438	1.4325	500
520	812.4	0.0209	0.5385	0.5594	511.9	686.4	1198.2	0.7130	0.7006	1.4136	520
540	962.5	0.0215	0.4434	0.4649	536.6	656.6	1193.2	0.7374	0.6568	1.3942	540
560	1133.1	0.0221	0.3647	0.3868	562.2	624.2	1186.4	0.7621	0.6121	1.3742	560
580	1325.8	0.0228	0.2989	0.3217	588.9	588.4	1177.3	0.7872	0.5659	1.3532	580
600	1542.9	0.0236	0.2432	0.2668	617.0	548.5	1165.5	0.8131	0.5176	1.3307	600
620	1786.6	0.0247	0.1955	0.2201	646.7	503.6	1150.3	0.8398	0.4664	1.3062	620
640	2059.7	0.0260	0.1538	0.1798	678.6	452.0	1130.5	0.8679	0.4110	1.2789	640
660	2365.4	0.0278	0.1165	0.1442	714.2	390.2	1104.4	0.8987	0.3485	1.2472	660
680	2708.1	0.0305	0.0810	0.1115	757.3	309.9	1067.2	0.9351	0.2719	1.2071	680
700	3093.7	0.0369	0.0392	0.0761	823.3	172.1	995.4	0.9905	0.1484	1.1389	700
705.4	3206.2	0.0503	0	0.0503	902.7	0	902.7	1.0580	0	1.0580	705.4

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TABLE 2  
DRY SATURATED STEAM: PRESSURE TABLE \*

Abs Press., Lb Sq In. <i>p</i>	Temp., F <i>t</i>	Specific Volume		Enthalpy		Entropy		Internal Energy Sat. Liquid <i>u<sub>f</sub></i>	Internal Energy Sat. Vapor <i>u<sub>g</sub></i>	Abs Press., Lb Sq In. <i>p</i>
		Sat. Liquid <i>v<sub>f</sub></i>	Sat. Vapor <i>v<sub>g</sub></i>	Sat. Liquid <i>h<sub>f</sub></i>	Evap <i>h<sub>fg</sub></i>	Sat. Vapor <i>h<sub>g</sub></i>	Sat. Liquid <i>s<sub>f</sub></i>	Evap <i>s<sub>fg</sub></i>	Sat. Vapor <i>s<sub>g</sub></i>	
0.491	79.03	0.01608	652.3	47.05	1049.2	1096.3	0.0914	1.9473	2.0387	0.491
0.736	91.72	0.01611	444.9	59.71	1042.0	1101.7	0.1147	1.8894	2.0041	0.736
0.982	101.14	0.01614	339.2	69.10	1036.6	1105.7	0.1316	1.8481	1.9797	0.982
1.227	108.71	0.01616	274.9	76.65	1032.3	1108.9	0.1449	1.8160	1.9609	1.227
1.473	115.06	0.01618	231.6	82.99	1028.6	1111.6	0.1560	1.7896	1.9456	1.473
1.964	125.43	0.01622	176.7	93.34	1022.7	1116.0	0.1738	1.7476	1.9214	1.964
2.455	133.76	0.01626	143.25	101.66	1017.7	1119.4	0.1879	1.7150	1.9028	2.455
5	162.24	0.01640	73.52	130.13	1001.0	1131.1	0.2347	1.6094	1.8441	5
10	193.21	0.01659	38.42	161.17	982.1	1143.3	0.2835	1.5041	1.7876	10
14.696	212.0	0.01672	26.80	180.07	970.3	1150.4	0.3120	1.4446	1.7566	14.696
15	213.03	0.01672	26.29	181.11	969.7	1150.8	0.3135	1.4415	1.7549	15
16	216.32	0.01674	24.75	184.42	967.6	1152.0	0.3184	1.4313	1.7497	16
18	222.41	0.01679	22.17	190.56	963.6	1154.2	0.3275	1.4128	1.7403	18
20	227.96	0.01683	20.089	196.16	960.1	1156.3	0.3356	1.3962	1.7319	20
25	240.07	0.01692	16.303	208.42	952.1	1160.6	0.3533	1.3606	1.7139	25
30	250.33	0.01701	13.746	218.82	945.3	1164.1	0.3680	1.3313	1.6993	30
35	259.28	0.01708	11.898	227.91	939.2	1167.1	0.3807	1.3063	1.6870	35
40	267.25	0.01715	10.498	236.03	933.7	1169.7	0.3919	1.2844	1.6763	40
45	274.44	0.01721	9.401	243.36	928.6	1172.0	0.4019	1.2650	1.6669	45
50	281.01	0.01727	8.515	250.09	924.0	1174.1	0.4110	1.2474	1.6585	50
55	287.07	0.01732	7.787	256.30	919.6	1175.9	0.4193	1.2316	1.6509	55
60	292.71	0.01738	7.175	262.09	915.5	1177.6	0.4270	1.2168	1.6438	60
65	297.97	0.01743	6.655	267.50	911.6	1179.1	0.4342	1.2032	1.6374	65
70	302.92	0.01748	6.206	272.61	907.9	1180.6	0.4409	1.1906	1.6315	70
75	307.60	0.01753	5.816	277.43	904.5	1181.9	0.4472	1.1787	1.6259	75
80	312.03	0.01757	5.472	282.02	901.1	1183.1	0.4531	1.1676	1.6207	80
85	316.25	0.01761	5.168	286.39	897.8	1184.2	0.4587	1.1571	1.6158	85
90	320.27	0.01766	4.896	290.56	894.7	1185.3	0.4641	1.1471	1.6112	90
100	327.81	0.01774	4.432	298.40	888.8	1187.2	0.4740	1.1286	1.6026	100
110	334.77	0.01782	4.049	305.66	883.2	1188.9	0.4832	1.1117	1.5948	110



120	341.25	0.01789	3.728	312.44	877.9	1190.4	0.4916	1.0962	1.5878	312.05	1107.6	120
130	347.32	0.01796	3.455	318.81	872.9	1191.7	0.4995	1.0817	1.5812	318.38	1108.6	130
140	353.02	0.01802	3.220	324.82	868.2	1193.0	0.5069	1.0682	1.5751	324.35	1109.6	140
150	358.42	0.01809	3.015	330.51	863.6	1194.1	0.5138	1.0556	1.5694	330.01	1110.5	150
160	363.53	0.01815	2.834	335.93	859.2	1195.1	0.5204	1.0436	1.5640	335.39	1111.2	160
170	368.41	0.01822	2.675	341.09	854.9	1196.0	0.5266	1.0324	1.5590	340.52	1111.9	170
180	373.06	0.01827	2.532	346.03	850.8	1196.9	0.5325	1.0217	1.5542	345.42	1112.5	180
190	377.51	0.01833	2.404	350.79	846.8	1197.6	0.5381	1.0116	1.5497	350.15	1113.1	190
200	381.79	0.01839	2.288	355.36	843.0	1198.4	0.5435	1.0018	1.5453	354.68	1113.7	200
250	400.95	0.01865	1.8438	376.00	825.1	1201.1	0.5675	0.9588	1.5263	375.14	1115.8	250
300	417.33	0.01890	1.5433	393.84	809.0	1202.8	0.5879	0.9225	1.5104	392.79	1117.1	300
350	431.72	0.01913	1.3260	409.69	794.2	1203.9	0.6056	0.8910	1.4966	408.45	1118.0	350
400	444.59	0.0193	1.1613	424.0	780.5	1204.5	0.6214	0.8630	1.4844	422.6	1118.5	400
450	456.28	0.0195	1.0320	437.2	767.4	1204.6	0.6356	0.8378	1.4734	435.5	1118.7	450
500	467.01	0.0197	0.9278	449.4	755.0	1204.4	0.6487	0.8147	1.4634	447.6	1118.6	500
550	476.94	0.0199	0.8424	460.8	743.1	1203.9	0.6608	0.7934	1.4542	458.8	1118.2	550
600	486.21	0.0201	0.7698	471.6	731.6	1203.2	0.6720	0.7734	1.4454	469.4	1117.7	600
650	494.90	0.0203	0.7083	481.8	720.5	1202.3	0.6826	0.7548	1.4374	479.4	1117.1	650
700	503.10	0.0205	0.6554	491.5	709.7	1201.2	0.6925	0.7371	1.4296	488.8	1116.3	700
750	510.86	0.0207	0.6092	500.8	699.2	1200.0	0.7019	0.7204	1.4223	598.0	1115.4	750
800	518.23	0.0209	0.5687	509.7	688.9	1198.6	0.7108	0.7045	1.4153	506.6	1114.4	800
850	525.26	0.0210	0.5327	518.3	678.8	1197.1	0.7194	0.6891	1.4085	515.0	1113.3	850
900	531.98	0.0212	0.5006	526.6	668.8	1195.4	0.7275	0.6744	1.4020	523.1	1112.1	900
950	538.43	0.0214	0.4717	534.6	659.1	1193.7	0.7355	0.6602	1.3957	530.9	1110.8	950
1000	544.61	0.0216	0.4456	542.4	649.4	1191.8	0.7430	0.6467	1.3897	538.4	1109.4	1000
1100	556.31	0.0220	0.4001	557.4	630.4	1187.8	0.7575	0.6205	1.3780	552.9	1106.4	1100
1200	567.22	0.0223	0.3619	571.7	611.7	1183.4	0.7711	0.5956	1.3667	566.7	1103.0	1200
1300	577.46	0.0227	0.3293	585.4	593.2	1178.6	0.7840	0.5719	1.3559	580.0	1099.4	1300
1400	587.10	0.0231	0.3012	598.7	574.7	1173.4	0.7963	0.5491	1.3454	592.7	1095.4	1400
1500	596.23	0.0235	0.2765	611.6	556.3	1167.9	0.8082	0.5269	1.3351	605.1	1091.2	1500
2000	635.82	0.0257	0.1878	671.7	463.4	1135.1	0.8619	0.4230	1.2849	662.2	1065.6	2000
2500	668.13	0.0287	0.1307	730.6	360.5	1091.1	0.9126	0.3197	1.2322	717.3	1030.6	2500
3000	695.36	0.0346	0.0858	802.5	217.8	1020.3	0.9731	0.1885	1.1615	783.4	972.7	3000
3206.2	705.40	0.0503	0.0503	902.7	0	902.7	1.0580	0	1.0580	872.9	872.9	3206.2

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TABLE 3  
PROPERTIES OF SUPERHEATED STEAM \*

Abs Press., Lb Sq In. (Sat. Temp.)		Temperature—Degrees Fahrenheit												
		200	220	300	350	400	450	500	550	600	700	800	900	1000
1 (101.74)	v.....	392.6	404.5	452.3	482.2	512.0	541.8	571.6	601.4	631.2	690.8	750.4	809.9	869.5
	h.....	1150.4	1159.5	1195.8	1218.7	1241.7	1264.9	1288.3	1312.0	1335.7	1383.8	1432.8	1482.7	1533.5
	s.....	2.0512	2.0647	2.1153	2.1444	2.1720	2.1983	2.2233	2.2468	2.2702	2.3137	2.3542	2.3923	2.4283
5 (162.24)	v.....	78.16	80.59	90.25	96.26	102.26	108.24	114.22	120.19	126.16	138.10	150.03	161.95	173.87
	h.....	1148.8	1158.1	1195.0	1218.1	1241.2	1264.5	1288.0	1311.7	1335.4	1383.6	1432.7	1482.6	1533.4
	s.....	1.8718	1.8857	1.9370	1.9664	1.9942	2.0205	2.0456	2.0692	2.0927	2.1361	2.1767	2.2148	2.2509
10 (193.21)	v.....	38.85	40.09	45.00	48.03	51.04	54.05	57.05	60.04	63.03	69.01	74.98	80.95	86.92
	h.....	1146.6	1156.2	1193.9	1217.2	1240.6	1264.0	1287.5	1311.3	1335.1	1383.4	1432.5	1482.4	1533.2
	s.....	1.7927	1.8071	1.8595	1.8892	1.9172	1.9436	1.9689	1.9924	2.0160	2.0596	2.1002	2.1383	2.1744
14.696 (212.00)	v.....	.....	27.15	30.53	32.62	34.68	36.73	38.78	40.82	42.86	46.94	51.00	55.07	59.13
	h.....	.....	1154.4	1192.8	1216.4	1239.9	1263.5	1287.1	1310.9	1334.8	1383.2	1432.3	1482.3	1533.1
	s.....	.....	1.7624	1.8160	1.8460	1.8743	1.9008	1.9261	1.9498	1.9734	2.0170	2.0576	2.0958	2.1319
20 (227.96)	v.....	.....	.....	22.36	23.91	25.43	26.95	28.46	29.97	31.47	34.47	37.46	40.45	43.44
	h.....	.....	.....	1191.6	1215.6	1239.2	1262.9	1286.6	1310.5	1334.4	1382.9	1432.1	1482.1	1533.0
	s.....	.....	.....	1.7808	1.8112	1.8396	1.8664	1.8918	1.9160	1.9392	1.9829	2.0235	2.0618	2.0978
40 (267.25)	v.....	.....	.....	11.040	11.843	12.628	13.401	14.168	14.93	15.688	17.198	18.702	20.20	21.70
	h.....	.....	.....	1186.8	1211.9	1236.5	1260.7	1284.8	1308.9	1333.1	1381.9	1431.3	1481.4	1532.4
	s.....	.....	.....	1.6994	1.7314	1.7608	1.7881	1.8140	1.8384	1.8619	1.9058	1.9467	1.9850	2.0214
60 (292.71)	v.....	.....	.....	7.259	7.818	8.357	8.884	9.403	9.916	10.427	11.441	12.449	13.452	14.454
	h.....	.....	.....	1181.6	1208.2	1233.6	1258.5	1283.0	1307.4	1331.8	1380.9	1430.5	1480.8	1531.9
	s.....	.....	.....	1.6492	1.6830	1.7135	1.7416	1.7678	1.7926	1.8162	1.8605	1.9015	1.9400	1.9762
80 (312.03)	v.....	.....	.....	.....	5.803	6.22	6.624	7.020	7.410	7.797	8.562	9.322	10.077	10.830
	h.....	.....	.....	.....	1204.3	1230.7	1256.1	1281.1	1305.8	1330.5	1379.9	1429.7	1480.1	1531.3
	s.....	.....	.....	.....	1.6475	1.6791	1.7078	1.7346	1.7598	1.7836	1.8281	1.8694	1.9079	1.9442
100 (327.81)	v.....	.....	.....	.....	4.592	4.937	5.268	5.589	5.905	6.218	6.835	7.446	8.052	8.656
	h.....	.....	.....	.....	1200.1	1227.6	1253.7	1279.1	1304.2	1329.1	1378.9	1428.9	1479.5	1530.8
	s.....	.....	.....	.....	1.6188	1.6518	1.6813	1.7085	1.7339	1.7581	1.8029	1.8443	1.8829	1.9193
120 (341.25)	v.....	.....	.....	.....	3.783	4.081	4.363	4.636	4.902	5.165	5.683	6.195	6.702	7.207
	h.....	.....	.....	.....	1195.7	1224.4	1251.3	1277.2	1302.5	1327.7	1377.8	1428.1	1478.8	1530.2
	s.....	.....	.....	.....	1.5944	1.6287	1.6591	1.6869	1.7127	1.7370	1.7822	1.8237	1.8625	1.8990



<b>140</b> (353.02)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	3.468 1221.1 1.6087	3.715 1248.7 1.6515	3.954 1275.2 1.6683	4.186 1300.9 1.6945	4.413 1326.4 1.7190	4.861 1376.8 1.7645	5.301 1427.3 1.8063	5.738 1478.2 1.8451	6.172 1529.7 1.8817
<b>160</b> (363.53)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	3.008 1217.6 1.5908	3.230 1246.1 1.6230	3.443 1273.1 1.6519	3.648 1299.3 1.6785	3.849 1325.0 1.7033	4.244 1375.7 1.7491	4.631 1426.4 1.7911	5.015 1477.5 1.8301	5.396 1529.1 1.8667
<b>180</b> (373.06)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	2.649 1214.0 1.5745	2.852 1248.5 1.6077	3.044 1271.0 1.6373	3.229 1297.6 1.6642	3.411 1323.5 1.6894	3.764 1374.7 1.7355	4.110 1425.6 1.7776	4.452 1476.8 1.8167	4.792 1528.6 1.8534
<b>200</b> (381.79)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	2.361 1210.3 1.5594	2.549 1240.7 1.5937	2.726 1268.9 1.6240	2.895 1295.8 1.6513	3.060 1322.1 1.6767	3.380 1373.6 1.7232	3.693 1424.8 1.7655	4.002 1476.2 1.8048	4.309 1528.0 1.8415
<b>220</b> (389.86)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	2.125 1206.5 1.5453	2.301 1237.9 1.5808	2.465 1266.7 1.6117	2.621 1294.1 1.6395	2.772 1320.7 1.6652	3.066 1372.6 1.7120	3.352 1424.0 1.7545	3.634 1475.5 1.7939	3.913 1527.5 1.8308
<b>240</b> (397.37)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	1.9276 1202.5 1.5319	2.1120 1234.9 1.5686	2.247 1264.5 1.6003	2.393 1292.4 1.6286	2.533 1319.2 1.6546	2.804 1371.5 1.7017	3.068 1423.2 1.7444	3.327 1474.8 1.7839	3.584 1526.9 1.8209
<b>260</b> (404.42)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	..... ..... .....	1.9183 1232.0 1.5573	2.063 1262.3 1.5897	2.199 1290.5 1.6184	2.330 1317.7 1.6447	2.582 1370.4 1.6922	2.827 1422.3 1.7352	3.067 1474.2 1.7748	3.305 1526.3 1.8118
<b>280</b> (411.05)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	..... ..... .....	1.7674 1228.9 1.5464	1.9047 1260.0 1.5796	2.033 1288.7 1.6087	2.156 1316.2 1.6354	2.392 1369.4 1.6834	2.621 1421.5 1.7265	2.845 1473.5 1.7662	3.066 1525.8 1.8033
<b>300</b> (417.33)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	..... ..... .....	1.6364 1225.8 1.5360	1.7675 1257.6 1.5701	1.8891 1286.8 1.5998	2.005 1314.7 1.6268	2.227 1368.3 1.6751	2.442 1420.6 1.7184	2.652 1472.8 1.7582	2.859 1525.2 1.7954
<b>350</b> (431.72)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	..... ..... .....	1.3734 1217.7 1.5119	1.4923 1251.5 1.5481	1.6010 1282.1 1.5792	1.7036 1310.9 1.6070	1.8980 1365.5 1.6563	2.084 1418.5 1.7002	2.266 1471.1 1.7403	2.445 1523.8 1.7777
<b>400</b> (444.59)	$v$ ..... $h$ ..... $s$ .....	..... ..... .....	..... ..... .....	..... ..... .....	..... ..... .....	1.1744 1208.8 1.4892	1.2851 1245.1 1.5281	1.3843 1277.2 1.5607	1.4770 1306.9 1.5894	1.6508 1362.7 1.6398	1.8161 1416.4 1.6842	1.9767 1469.4 1.7247	2.134 1522.4 1.7623

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1400 (587.10)	<i>v</i> .....	0.3174	0.3390	0.3580	0.3753	0.3912	0.4062	0.4714	0.5281	0.5805	0.6789	0.7727	0.8640
	<i>h</i> .....	1193.0	1218.4	1240.4	1260.3	1278.5	1295.5	1369.1	1433.1	1493.2	1608.9	1723.7	1840.0
	<i>s</i> .....	1.3639	1.3877	1.4079	1.4258	1.4419	1.4567	1.5177	1.5666	1.6093	1.6836	1.7489	1.8083
1600 (604.90)	<i>v</i> .....	.....	0.2733	0.2936	0.3112	0.3271	0.3417	0.4034	0.4553	0.5027	0.5906	0.6738	0.7545
	<i>h</i> .....	.....	1187.8	1215.2	1238.7	1259.6	1278.7	1358.4	1425.3	1487.0	1604.6	1720.5	1837.5
	<i>s</i> .....	.....	1.3489	1.3741	1.3952	1.4137	1.4303	1.4964	1.5476	1.5914	1.6669	1.7328	1.7926
1800 (621.03)	<i>v</i> .....	.....	.....	0.2407	0.2597	0.2760	0.2907	0.3502	0.3986	0.4421	0.5218	0.5968	0.6693
	<i>h</i> .....	.....	.....	1185.1	1214.0	1238.5	1260.3	1347.2	1417.4	1480.8	1600.4	1717.3	1835.0
	<i>s</i> .....	.....	.....	1.3377	1.3638	1.3855	1.4044	1.4765	1.5301	1.5752	1.6520	1.7185	1.7786
2000 (635.82)	<i>v</i> .....	.....	.....	0.1936	0.2161	0.2337	0.2489	0.3074	0.3532	0.3935	0.4668	0.5352	0.6011
	<i>h</i> .....	.....	.....	1145.6	1184.9	1214.8	1240.0	1335.5	1409.2	1474.5	1596.1	1714.1	1832.5
	<i>s</i> .....	.....	.....	1.2945	1.3300	1.3564	1.3783	1.4576	1.5139	1.5603	1.6384	1.7055	1.7660
2500 (668.13)	<i>v</i> .....	.....	.....	.....	.....	0.1484	0.1686	0.2294	0.2710	0.3061	0.3678	0.4244	0.4784
	<i>h</i> .....	.....	.....	.....	.....	1132.3	1176.8	1303.6	1387.8	1458.4	1585.3	1706.1	1826.2
	<i>s</i> .....	.....	.....	.....	.....	1.2687	1.3073	1.4127	1.4772	1.5273	1.6088	1.6775	1.7389
3000 (695.36)	<i>v</i> .....	.....	.....	.....	.....	.....	0.0984	0.1760	0.2159	0.2476	0.3018	0.3505	0.3966
	<i>h</i> .....	.....	.....	.....	.....	.....	1060.7	1267.2	1365.0	1441.8	1574.3	1698.0	1819.9
	<i>s</i> .....	.....	.....	.....	.....	.....	1.1966	1.3690	1.4439	1.4984	1.5837	1.6540	1.7163
3206.2 (705.40)	<i>v</i> .....	.....	.....	.....	.....	.....	.....	0.1583	0.1981	0.2288	0.2806	0.3267	0.3703
	<i>h</i> .....	.....	.....	.....	.....	.....	.....	1250.5	1355.2	1434.7	1569.8	1694.6	1817.2
	<i>s</i> .....	.....	.....	.....	.....	.....	.....	1.3508	1.4309	1.4874	1.5742	1.6452	1.7080
3500	<i>v</i> .....	.....	.....	.....	.....	.....	0.0306	0.1364	0.1762	0.2058	0.2546	0.2977	0.3381
	<i>h</i> .....	.....	.....	.....	.....	.....	780.5	1224.9	1340.7	1424.5	1563.3	1689.8	1813.6
	<i>s</i> .....	.....	.....	.....	.....	.....	0.9515	1.3241	1.4127	1.4723	1.5615	1.6336	1.6968
4000	<i>v</i> .....	.....	.....	.....	.....	.....	0.0287	0.1052	0.1462	0.1743	0.2192	0.2581	0.2943
	<i>h</i> .....	.....	.....	.....	.....	.....	763.8	1174.8	1314.4	1406.8	1552.1	1681.7	1807.2
	<i>s</i> .....	.....	.....	.....	.....	.....	0.9347	1.2757	1.3827	1.4482	1.5417	1.6154	1.6795
4500	<i>v</i> .....	.....	.....	.....	.....	.....	0.0276	0.0798	0.1226	0.1500	0.1917	0.2273	0.2602
	<i>h</i> .....	.....	.....	.....	.....	.....	753.5	1113.9	1286.5	1388.4	1540.8	1673.5	1800.9
	<i>s</i> .....	.....	.....	.....	.....	.....	0.9235	1.2204	1.3529	1.4253	1.5235	1.5990	1.6640
5000	<i>v</i> .....	.....	.....	.....	.....	.....	0.0268	0.0593	0.1036	0.1303	0.1696	0.2027	0.2329
	<i>h</i> .....	.....	.....	.....	.....	.....	746.4	1047.1	1256.5	1369.5	1529.5	1665.3	1794.5
	<i>s</i> .....	.....	.....	.....	.....	.....	0.9152	1.1622	1.3231	1.4034	1.5066	1.5839	1.6499
5500	<i>v</i> .....	.....	.....	.....	.....	.....	0.0262	0.0463	0.0880	0.1143	0.1516	0.1825	0.2106
	<i>h</i> .....	.....	.....	.....	.....	.....	741.3	985.0	1224.1	1349.3	1518.2	1657.0	1788.1
	<i>s</i> .....	.....	.....	.....	.....	.....	0.9090	1.1093	1.2930	1.3821	1.4908	1.5699	1.6369

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TABLE 4. PROPERTIES OF MERCURY VAPOR\*  
( $h$  and  $s$  are measured from 32 F.)

Pres- sure $p$ psia	Temp $t$ , F	Specific volume $v_g$ $\text{ft}^3 \text{lb}_m^{-1}$	Enthalpy, Btu $\text{lb}_m^{-1}$			Entropy, Btu $\text{lb}_m^{-1} \text{R}^{-1}$		
			Satu- rated liquid $h_f$	Vapor- ization $h_{fg}$	Satu- rated vapor $h_g$	Satu- rated liquid $s_f$	Vapor- ization $s_{fg}$	Satu- rated vapor $s_g$
0.4	402.3	114.5	13.81	128.1	141.9	0.02094	0.1486	0.1696
0.6	426.1	78.23	14.70	127.6	142.3	0.02195	0.1441	0.1660
0.8	443.8	59.71	15.36	127.2	142.6	0.02269	0.1408	0.1635
1.0	458.1	48.45	15.89	126.9	142.8	0.02328	0.1382	0.1615
1.5	485.1	33.14	16.90	126.3	143.2	0.02436	0.1337	0.1580
2	505.2	25.31	17.65	125.8	143.5	0.02514	0.1304	0.1556
3	535.4	17.34	18.78	125.2	144.0	0.02629	0.1258	0.1521
4	558.0	13.26	19.62	124.7	144.3	0.02714	0.1225	0.1497
5	576.2	10.77	20.30	124.3	144.6	0.02780	0.1200	0.1478
6	591.4	9.096	20.87	123.9	144.8	0.02834	0.1179	0.1462
7	605.0	7.882	21.37	123.6	145.0	0.02882	0.1161	0.1450
8	616.8	6.963	21.81	123.4	145.2	0.02923	0.1146	0.1439
9	627.5	6.244	22.21	123.2	145.4	0.02960	0.1133	0.1429
10	637.3	5.661	22.58	122.9	145.5	0.02993	0.1121	0.1420
15	676.5	3.892	24.04	122.1	146.1	0.03124	0.1074	0.1387
20	706.2	2.983	25.15	121.4	146.6	0.03220	0.1041	0.1363
25	730.4	2.429	26.05	120.9	146.9	0.03297	0.1016	0.1345
30	750.9	2.053	26.81	120.4	147.2	0.03360	0.09953	0.1331
35	769.0	1.781	27.49	120.0	147.5	0.03416	0.09774	0.1319
40	784.8	1.576	28.08	119.7	147.8	0.03464	0.09621	0.1308
45	799.3	1.414	28.62	119.4	148.0	0.03507	0.09486	0.1299
50	812.5	1.284	29.11	119.1	148.2	0.03546	0.09364	0.1291
60	836.1	1.086	29.99	118.6	148.6	0.03614	0.09154	0.1276
70	856.6	0.9436	30.75	118.1	148.9	0.03672	0.08976	0.1264
80	874.8	0.8349	31.43	117.7	149.1	0.03725	0.08824	0.1254
90	891.6	0.7497	32.06	117.3	149.4	0.03771	0.08687	0.1245
100	906.9	0.6811	32.63	117.0	149.6	0.03813	0.08565	0.1237
120	934.4	0.5767	33.60	116.4	150.1	0.03887	0.08353	0.1224
140	958.3	0.5012	34.55	115.9	150.4	0.03951	0.08175	0.1212
160	979.9	0.4438	35.35	115.4	150.8	0.04007	0.08019	0.1202
180	999.6	0.3990	36.09	115.0	151.1	0.04058	0.07881	0.1193

\* Reproduced from L. S. Marks, "Mechanical Engineers' Handbook," McGraw-Hill Book Company, Inc., New York.



TABLE 5. PROPERTIES OF SATURATED AMMONIA<sup>1</sup>  
(Entropy and enthalpy measurements are from -40°F.)

Temp., °F.  <i>t</i>	Pres- sure, lb. per sq. in. abs.  <i>p</i>	Specific volume, cu. ft. per lb.		Enthalpy of liquid  <i>h<sub>f</sub></i>	Enthalpy of vaporiz- ation  <i>h<sub>fg</sub></i>	Enthalpy of vapor  <i>h<sub>g</sub></i>	Entropy		
		Liquid  <i>v<sub>f</sub></i>	Vapor  <i>v<sub>g</sub></i>				of liquid  <i>s<sub>f</sub></i>	of evap.  <i>s<sub>fg</sub></i>	of vapor  <i>s<sub>g</sub></i>
-40	10.41	0.02322	24.86	0.0	597.6	597.6	0.000	1.4242	1.4242
-38	11.04	0.02326	23.53	2.1	596.2	598.3	0.0051	1.4142	1.4193
-36	11.71	0.02331	22.27	4.3	594.8	599.1	0.0101	1.4043	1.4144
-34	12.41	0.02335	21.10	6.4	593.5	599.9	0.0151	1.3945	1.4096
-32	13.14	0.02340	20.00	8.5	592.1	600.6	0.0201	1.3847	1.4048
-30	13.90	0.02345	18.97	10.7	590.7	601.4	0.0250	1.3751	1.4001
-28	14.71	0.02349	18.00	12.8	589.3	602.1	0.0300	1.3655	1.3955
-26	15.55	0.02354	17.09	14.9	587.9	602.8	0.0350	1.3559	1.3909
-24	16.42	0.02359	16.24	17.1	586.5	603.6	0.0399	1.3464	1.3863
-22	17.34	0.02364	15.43	19.2	585.1	604.3	0.0448	1.3370	1.3818
-20	18.30	0.02369	14.68	21.4	583.6	605.0	0.0497	1.3277	1.3774
-18	19.30	0.02374	13.97	23.5	582.2	605.7	0.0545	1.3184	1.3729
-16	20.34	0.02378	13.29	25.6	580.8	606.4	0.0594	1.3092	1.3686
-14	21.43	0.02383	12.66	27.8	579.3	607.1	0.0642	1.3001	1.3643
-12	22.56	0.02384	12.06	30.0	577.8	607.8	0.0690	1.2910	1.3600
-10	23.74	0.02393	11.50	32.1	576.4	608.5	0.0738	1.2820	1.3558
- 8	24.97	0.02399	10.97	34.3	574.9	609.2	0.0786	1.2730	1.3516
- 6	26.26	0.02404	10.47	36.4	573.4	609.8	0.0833	1.2641	1.3474
- 4	27.59	0.02409	9.991	38.6	571.9	610.5	0.0880	1.2553	1.3433
- 2	28.98	0.02414	9.541	40.7	570.4	611.1	0.0928	1.2465	1.3393
0	30.42	0.02419	9.116	42.9	568.9	611.8	0.0975	1.2377	1.3352
2	31.92	0.02424	8.714	45.1	567.3	612.4	0.1022	1.2290	1.3312
4	33.47	0.02430	8.333	47.2	565.8	613.0	0.1069	1.2204	1.3273
6	35.09	0.02435	7.971	49.4	564.2	613.6	0.1115	1.2119	1.3234
8	36.77	0.02440	7.629	51.6	562.7	614.3	0.1162	1.2033	1.3195
10	38.51	0.02446	7.304	53.8	561.1	614.9	0.1208	1.1949	1.3157
12	40.31	0.02451	6.996	56.0	559.5	615.5	0.1254	1.1864	1.3118
14	42.18	0.02457	6.703	58.2	557.9	616.1	0.1300	1.1781	1.3081
16	44.12	0.02462	6.425	60.3	556.3	616.6	0.1346	1.1697	1.3043
18	46.13	0.02468	6.161	62.5	554.7	617.2	0.1392	1.1614	1.3006
20	48.21	0.02474	5.910	64.7	553.1	617.8	0.1437	1.1532	1.2969
22	50.36	0.02479	5.671	66.9	551.4	618.3	0.1483	1.1450	1.2933
24	52.59	0.02485	5.443	69.1	549.8	618.9	0.1528	1.1369	1.2897
26	54.90	0.02491	5.227	71.3	548.1	619.4	0.1573	1.1288	1.2861
28	57.28	0.02497	5.021	73.5	546.4	619.9	0.1618	1.1207	1.2825
30	59.74	0.02503	4.825	75.7	544.8	620.5	0.1663	1.1127	1.2790
32	62.29	0.02508	4.637	77.9	543.1	621.0	0.1708	1.1047	1.2755
34	64.91	0.02514	4.459	80.1	541.4	621.5	0.1753	1.0968	1.2721
36	67.63	0.02521	4.289	82.3	539.7	622.0	0.1797	1.0889	1.2686
38	70.43	0.02527	4.126	84.6	537.9	622.5	0.1841	1.0811	1.2652
40	73.32	0.02533	3.971	86.8	536.2	623.0	0.1885	1.0733	1.2618
42	76.31	0.02539	3.823	89.0	534.4	623.4	0.1930	1.0655	1.2585
44	79.38	0.02545	3.682	91.2	532.7	623.9	0.1974	1.0578	1.2552
46	82.55	0.02551	3.547	93.5	530.9	624.4	0.2018	1.0501	1.2519
48	85.82	0.02558	3.418	95.7	529.1	624.8	0.2062	1.0424	1.2486
50	89.19	0.02564	3.294	97.9	527.3	625.2	0.2105	1.0348	1.2453
52	92.66	0.02571	3.176	100.2	525.5	625.7	0.2149	1.0272	1.2421
54	96.23	0.02577	3.063	102.4	523.7	626.1	0.2192	1.0197	1.2389
56	99.91	0.02584	2.954	104.7	521.8	626.5	0.2236	1.0121	1.2357
58	103.7	0.02590	2.851	106.9	520.0	626.9	0.2279	1.0046	1.2325
60	107.6	0.02597	2.751	109.2	518.1	627.3	0.2322	0.9972	1.2294
62	111.6	0.02604	2.656	111.5	516.2	627.7	0.2365	0.9897	1.2262
64	115.7	0.02611	2.565	113.7	514.3	628.0	0.2408	0.9823	1.2231
66	120.0	0.02618	2.477	116.0	512.4	628.4	0.2451	0.9750	1.2201
68	124.3	0.02625	2.393	118.3	510.5	628.8	0.2494	0.9676	1.2170
70	128.8	0.02632	2.312	120.5	508.6	629.1	0.2537	0.9603	1.2140
72	133.4	0.02639	2.235	122.8	506.6	629.4	0.2579	0.9531	1.2110
74	138.1	0.02646	2.161	125.1	504.7	629.8	0.2622	0.9458	1.2080
76	143.0	0.02653	2.089	127.4	502.7	630.1	0.2664	0.9386	1.2050
78	147.9	0.02661	2.021	129.7	500.7	630.4	0.2706	0.9314	1.2020
80	153.0	0.02668	1.955	132.0	498.7	630.7	0.2749	0.9242	1.1991
82	158.3	0.02675	1.892	134.3	496.7	631.0	0.2791	0.9171	1.1962
84	163.7	0.02684	1.831	136.6	494.7	631.3	0.2833	0.9100	1.1933
86	169.2	0.02691	1.772	138.9	492.6	631.5	0.2875	0.9029	1.1904
88	174.8	0.02699	1.716	141.2	490.6	631.8	0.2917	0.8958	1.1875
90	180.6	0.02707	1.661	143.5	488.5	632.0	0.2958	0.8888	1.1846
92	186.6	0.02715	1.609	145.8	486.4	632.2	0.3000	0.8818	1.1818
94	192.7	0.02723	1.559	148.2	484.3	632.5	0.3041	0.8748	1.1789
96	198.9	0.02731	1.510	150.5	482.1	632.6	0.3083	0.8678	1.1761
98	205.3	0.02739	1.464	152.9	480.0	632.9	0.3125	0.8608	1.1733
100	211.9	0.02747	1.419	155.2	477.8	633.0	0.3166	0.8539	1.1705
105	228.9	0.02769	1.313	161.1	472.3	633.4	0.3269	0.8366	1.1635
110	247.0	0.02790	1.217	167.0	466.7	633.7	0.3372	0.8194	1.1566
115	266.2	0.02813	1.128	173.0	460.9	633.9	0.3474	0.8023	1.1497
120	286.4	0.02836	1.047	179.0	455.0	634.0	0.3576	0.7851	1.1427

<sup>1</sup> Marks, "Mechanical Engineers' Handbook."

TABLE 6. PROPERTIES OF SUPERHEATED AMMONIA<sup>1</sup>  
(Condensed from *Circular* No. 142 of the U. S. Bureau of Standards, 1923)  
*v* = specific volume in cu. ft. per lb.; *h* = enthalpy in B.t.u. per lb.;  
*s* = entropy.  
(*h* and *s* are measured from −40°F.)

Pressure lb. per sq. in. abs.	Temp. of satu- rated vapor, °F.	Temperature of superheated vapor, °F.									
		−30	−20	−10	0	10	20	30	40	50	
10	−41.34	v	26.58	27.26	27.92	28.58	29.24	29.90	30.55	31.20	31.85
		h	603.2	608.5	613.7	618.9	624.0	629.1	634.2	639.3	644.4
		s	1.4420	1.4542	1.4659	1.4773	1.4884	1.4992	1.5097	1.5200	1.5301
20	−16.64	v	.....	.....	13.74	14.09	14.44	14.78	15.11	15.45	15.78
		h	.....	.....	610.0	615.5	621.0	626.4	631.7	637.0	642.3
		s	.....	.....	1.3784	1.3907	1.4025	1.4138	1.4240	1.4356	1.4460
30	− 0.57	v	.....	.....	.....	9.250	9.492	9.731	9.966	10.20	10.43
		h	.....	.....	.....	611.9	617.8	623.5	629.1	634.6	640.1
		s	.....	.....	.....	1.3371	1.3497	1.3618	1.3733	1.3845	1.3953
40	11.66	v	.....	.....	.....	.....	.....	7.203	7.387	7.568	7.746
		h	.....	.....	.....	.....	.....	620.4	626.3	632.1	637.8
		s	.....	.....	.....	.....	.....	1.3231	1.3353	1.3470	1.3583
50	21.67	v	.....	.....	.....	.....	.....	.....	5.838	5.988	6.135
		h	.....	.....	.....	.....	.....	.....	623.4	629.5	635.4
		s	.....	.....	.....	.....	.....	.....	1.3046	1.3169	1.3286
			100	120	140	160	180	200	240	280	320
80	44.40	v	4.190	4.371	4.548	4.722	4.893	5.063	5.398	5.730	.....
		h	658.7	670.4	681.8	693.2	704.4	715.6	738.1	760.7	.....
		s	1.3199	1.3404	1.3598	1.3784	1.3963	1.4136	1.4467	1.4781	.....
100	56.05	v	3.304	3.454	3.600	3.743	3.883	4.021	4.294	4.562	.....
		h	655.2	667.3	679.2	690.8	702.3	713.7	736.5	759.4	.....
		s	1.2891	1.3104	1.3305	1.3495	1.3678	1.3854	1.4190	1.4507	.....
120	66.02	v	2.712	2.842	2.967	3.089	3.209	3.326	3.557	3.783	.....
		h	651.6	664.2	676.5	688.5	700.2	711.8	734.9	758.0	.....
		s	1.2628	1.2850	1.3058	1.3254	1.3441	1.3620	1.3960	1.4281	.....
140	74.79	v	2.288	2.404	2.515	2.622	2.727	2.830	3.030	3.227	3.420
		h	647.8	661.1	673.7	686.0	698.0	709.9	733.3	756.7	780.0
		s	1.2396	1.2628	1.2843	1.3045	1.3236	1.3418	1.3763	1.4088	1.4395
160	82.64	v	1.969	2.075	2.175	2.272	2.365	2.457	2.635	2.809	2.980
		h	643.9	657.8	670.9	683.5	695.8	707.9	731.7	755.3	778.9
		s	1.2186	1.2429	1.2652	1.2859	1.3054	1.3240	1.3591	1.3919	1.4229
180	89.78	v	1.720	1.818	1.910	1.999	2.084	2.167	2.328	2.484	2.637
		h	639.9	654.4	668.0	681.0	693.6	705.9	730.1	753.9	777.7
		s	1.1992	1.2247	1.2477	1.2691	1.2891	1.3081	1.3436	1.3768	1.4081
200	96.34	v	1.520	1.612	1.698	1.780	1.859	1.935	2.082	2.225	2.364
		h	635.6	650.9	665.0	678.4	691.3	703.9	728.4	752.5	776.5
		s	1.1809	1.2077	1.2317	1.2537	1.2742	1.2935	1.3296	1.3631	1.3947
220	102.42	v	.....	1.443	1.525	1.601	1.675	1.745	1.881	2.012	2.140
		h	.....	647.3	662.0	675.8	689.1	701.9	726.8	751.1	775.3
		s	.....	1.1917	1.2167	1.2394	1.2604	1.2801	1.3168	1.3507	1.3825
240	108.09	v	.....	1.302	1.380	1.452	1.521	1.587	1.714	1.835	1.954
		h	.....	643.5	658.8	673.1	686.7	699.8	725.1	749.8	774.1
		s	.....	1.1764	1.2025	1.2259	1.2475	1.2677	1.3049	1.3392	1.3712
260	113.42	v	.....	1.182	1.257	1.326	1.391	1.453	1.572	1.686	1.796
		h	.....	639.5	655.6	670.4	684.4	697.7	723.4	748.4	772.9
		s	.....	1.1617	1.1889	1.2132	1.2354	1.2560	1.2938	1.3285	1.3608

<sup>1</sup> Marks, "Mechanical Engineers' Handbook."



TABLE 7.. PROPERTIES OF SATURATED SULPHUR DIOXIDE<sup>1</sup>  
(*h* and *s* are measured from  $-40^{\circ}\text{F.}$ )

Temp., °F.	Pres- sure, lb. per sq. in. abs.	Specific volume, cu. ft. per lb.		En- thalpy of liquid, B.t.u. per lb.	En- thalpy of vapori- zation, B.t.u.	En- thalpy of vapor, B.t.u.	Entropy		
		Liquid	Vapor				Of liquid	Of vapor- ization	Of vapor
<i>t</i>	<i>p</i>	<i>v<sub>f</sub></i>	<i>v<sub>g</sub></i>	<i>h<sub>f</sub></i>	<i>h<sub>fg</sub></i>	<i>h<sub>g</sub></i>	<i>s<sub>f</sub></i>	<i>s<sub>fg</sub></i>	<i>s<sub>g</sub></i>
-40	3.136	0.01044	22.42	0.00	178.6	178.6	0.0000	0.4256	0.4256
-30	4.331	0.01053	16.56	2.93	177.0	179.9	0.00674	0.4119	0.4186
-20	5.883	0.01062	12.42	5.98	175.1	181.1	0.01366	0.3983	0.4119
-10	7.863	0.01072	9.44	9.16	173.0	182.1	0.02075	0.3847	0.4054
0	10.35	0.01082	7.28	12.44	170.6	183.1	0.02795	0.3712	0.3992
10	13.42	0.01092	5.682	15.80	168.1	183.9	0.03519	0.3570	0.3931
20	17.18	0.01103	4.487	19.20	165.3	184.5	0.04241	0.3447	0.3871
30	21.70	0.01114	3.581	22.64	162.4	185.0	0.04956	0.3316	0.3812
40	27.10	0.01126	2.887	26.12	159.3	185.4	0.05668	0.3187	0.3754
50	33.45	0.01138	2.348	29.61	156.0	185.6	0.06370	0.3060	0.3697
60	40.93	0.01150	1.926	33.10	152.5	185.6	0.07060	0.2935	0.3641
70	49.62	0.01163	1.590	36.58	148.9	185.5	0.07736	0.2811	0.3585
80	59.68	0.01176	1.321	40.05	145.1	185.2	0.08399	0.2690	0.3529
90	71.25	0.01190	1.104	43.50	141.2	184.7	0.09038	0.2569	0.3473
100	84.52	0.01204	0.9262	46.90	137.2	184.1	0.09657	0.2452	0.3417
110	99.76	0.01219	0.7804	50.26	133.1	183.3	0.1025	0.2336	0.3361
120	120.9	0.01236	0.6598	53.58	128.8	182.4	0.1083	0.2222	0.3305
130	136.5	0.01253	0.5595	56.85	124.4	181.2	0.1138	0.2110	0.3247
140	158.6	0.01272	0.4758	60.04	119.9	179.9	0.1189	0.1999	0.3189

<sup>1</sup> Marks, "Mechanical Engineers' Handbook."

TABLE 8. PROPERTIES OF SUPERHEATED SULPHUR DIOXIDE<sup>1</sup>  
(*v* = specific volume in cu. ft. per lb.; *h* = enthalpy in B.t.u. per lb.;  
*s* = entropy)  
(*h* and *s* are measured from  $-40^{\circ}\text{F.}$ )

Pressure lb. per sq. in. abs.	Temp. of satu- rated vapor, °F.		Temperature of superheated vapor, °F.									
			0	20	40	60	80	100	120	140	160	
6	- 19.37	v	12.75	13.34	13.93	14.52	15.11	15.69	16.26	16.82	17.35	
		h	184.3	187.5	190.7	193.9	197.2	200.5	203.8	207.1	210.4	
		s	0.4185	0.4254	0.4320	0.4383	0.4444	0.4504	0.4561	0.4618	0.4672	
10	- 1.34	v	7.545	7.939	8.316	8.681	9.038	9.389	9.736	10.08	10.42	
		h	183.2	186.7	190.1	193.5	196.9	200.3	203.7	207.1	210.5	
		s	0.4005	0.4080	0.4151	0.4216	0.4280	0.4341	0.4400	0.4457	0.4512	
15	14.43	v	.....	5.192	5.470	5.734	5.988	6.233	6.471	6.705	6.937	
		h	.....	185.4	189.2	192.8	196.4	199.9	203.3	206.7	210.1	
		s	.....	0.3927	0.4005	0.4078	0.4144	0.4208	0.4268	0.4326	0.4383	
20	26.44	v	.....	.....	4.035	4.251	4.454	4.648	4.834	5.015	5.193	
		h	.....	.....	187.8	191.8	195.6	199.3	202.9	206.5	209.9	
		s	.....	.....	0.3896	0.3972	0.4043	0.4109	0.4173	0.4232	0.4290	
25	36.33	v	.....	.....	3.181	3.363	3.536	3.696	3.848	3.998	4.145	
		h	.....	.....	186.1	190.6	194.7	198.6	202.4	206.0	209.6	
		s	.....	.....	0.3793	0.3880	0.3958	0.4029	0.4095	0.4157	0.4216	
			60	80	100	120	140	160	180	200	220	
30	44.76	v	2.747	2.907	3.052	3.189	3.318	3.443	3.565	3.685	3.803	
		h	189.3	193.8	197.9	201.8	205.6	209.3	212.9	216.5	220.1	
		s	0.3797	0.3885	0.3960	0.4029	0.4094	0.4154	0.4211	0.4266	0.4318	
40	58.83	v	1.980	2.121	2.246	2.360	2.465	2.565	2.662	2.755	2.845	
		h	185.9	191.3	196.1	200.4	204.6	208.5	212.3	216.0	219.7	
		s	0.3654	0.3754	0.3842	0.3918	0.3988	0.4053	0.4113	0.4169	0.4223	
60	80.29	v	.....	.....	1.288	1.403	1.514	1.608	1.689	1.751	1.819	
		h	.....	.....	191.4	197.0	201.9	206.5	210.7	214.8	218.7	
		s	.....	.....	0.3640	0.3738	0.3822	0.3896	0.3964	0.4026	0.4084	
80	96.88	v	.....	.....	0.993	1.084	1.163	1.232	1.292	1.347	1.400	
		h	.....	.....	185.6	192.5	198.6	203.9	208.7	213.3	217.5	
		s	.....	.....	0.3457	0.3580	0.3682	0.3769	0.3846	0.3915	0.3978	

<sup>1</sup> Marks, "Mechanical Engineers' Handbook."



TABLE 9. PROPERTIES OF CARBON DIOXIDE<sup>1</sup>  
(Enthalpy measurements are from 32°F.)

Tem- pera- ture, °F.	Pres- sure, lb. per sq. in. abs.	Density, lb. per cu. ft.		B.t.u. per lb.			Entropy	
		of the liquid	of the vapor	Enthalpy of the liquid	Enthalpy of vapor- ization	Enthalpy of satu- rated vapor	of the liquid	of the vapor
		$\frac{1}{v_f}$	$\frac{1}{v_g}$	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_g$
<i>t</i>	<i>p</i>							
-40	145.87	69.8	1.64	-38.5	136.5	98.0	-0.0850	0.2400
-35	161.33	69.1	1.83	-35.8	134.3	98.5	-0.0793	0.2367
-30	177.97	68.3	2.02	-33.1	132.1	99.0	-0.0735	0.2336
-25	195.85	67.6	2.23	-30.4	129.8	99.4	-0.0676	0.2306
-20	215.02	66.9	2.44	-27.7	127.5	99.8	-0.0619	0.2277
-15	235.53	66.1	2.66	-24.9	125.0	100.1	-0.0560	0.2250
-10	257.46	65.3	2.91	-22.1	122.4	100.3	-0.0500	0.2220
- 5	280.85	64.5	3.17	-19.4	120.0	100.6	-0.0440	0.2198
0	305.76	63.6	3.46	-16.7	117.5	100.8	-0.0381	0.2173
5	332.2	62.8	3.77	-14.0	115.0	101.0	-0.0322	0.2151
10	360.4	61.9	4.12	-11.2	112.2	101.0	-0.0264	0.2124
15	390.2	61.0	4.49	- 8.4	109.4	101.0	-0.0204	0.2100
20	421.8	60.0	4.89	- 5.5	106.3	100.8	-0.0144	0.2071
25	455.3	59.0	5.33	- 2.5	103.1	100.6	-0.0083	0.2043
30	490.6	58.0	5.81	+ 0.4	99.7	100.1	-0.0021	0.2012
35	528.0	57.0	6.35	3.5	95.8	99.3	+0.0039	0.1975
40	567.3	55.9	6.91	6.6	91.8	98.4	0.0099	0.1934
45	608.9	54.7	7.60	9.8	87.5	97.3	0.0160	0.1892
50	652.7	53.4	8.37	12.9	83.2	96.1	0.0220	0.1852
55	698.8	52.1	9.27	16.1	78.7	94.8	0.0282	0.1809
60	747.4	50.7	10.2	19.4	74.0	93.4	0.0345	0.1767
65	798.6	49.1	11.3	22.9	68.9	91.8	0.0412	0.1724
70	852.4	47.3	12.6	26.6	62.7	89.3	0.0482	0.1665
75	909.3	45.1	14.2	30.9	54.8	85.7	0.0562	0.1587
80	969.3	42.4	16.2	35.6	44.0	79.6	0.0649	0.1464
85	1032.7	38.2	19.1	41.7	27.5	69.2	0.0761	0.1265
88	1072.1	32.9	25.4	Critical Point				

<sup>1</sup> Marks, "Mechanical Engineers' Handbook."

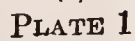
TABLE 10. PROPERTIES OF DICHLORODIFLUOROMETHANE (F-12-FREON)<sup>1</sup>  
(Entropy and enthalpy measurements are from −40°F.)

Temp., °F. <i>t</i>	Pressure, p.s.i. abs. <i>p</i>	Specific volume, cu. ft. per lb.		Enthalpy		Entropy	
		Liquid <i>v<sub>f</sub></i>	Vapor <i>v<sub>g</sub></i>	Liquid <i>h<sub>f</sub></i>	Vapor <i>h<sub>g</sub></i>	Liquid <i>s<sub>f</sub></i>	Vapor <i>s<sub>g</sub></i>
−40	9.33	0.0106	3.911	0	73.50	0	0.17517
−30	12.02	0.0107	3.088	2.03	74.70	0.00471	0.17387
−20	15.28	0.0108	2.474	4.07	75.87	0.00940	0.17275
−10	19.20	0.0109	2.003	6.14	77.05	0.01403	0.17175
0	23.87	0.0110	1.637	8.25	78.21	0.01869	0.17091
2	24.89	0.0111	1.574	8.67	78.44	0.01961	0.17075
4	25.96	0.0111	1.514	9.10	78.67	0.02052	0.17060
6	27.05	0.0111	1.457	9.53	78.90	0.02143	0.17045
8	28.18	0.0111	1.403	9.96	79.13	0.02235	0.17030
10	29.35	0.0112	1.351	10.39	79.36	0.02328	0.17015
12	30.56	0.0112	1.301	10.82	79.59	0.02419	0.17001
14	31.80	0.0112	1.253	11.26	79.82	0.02510	0.16987
16	33.08	0.0113	1.207	11.70	80.05	0.02601	0.16974
18	34.40	0.0113	1.163	12.12	80.27	0.02692	0.16961
20	35.75	0.0113	1.121	12.55	80.49	0.02783	0.16949
22	37.15	0.0113	1.081	13.00	80.72	0.02873	0.16938
24	38.58	0.0114	1.043	13.44	80.95	0.02963	0.16926
26	40.07	0.0114	1.007	13.88	81.17	0.03053	0.16913
28	41.59	0.0114	0.973	14.32	81.39	0.03143	0.16900
30	43.16	0.0115	0.939	14.76	81.61	0.03233	0.16887
32	44.77	0.0115	0.908	15.21	81.83	0.03323	0.16876
34	46.42	0.0115	0.877	15.65	82.05	0.03413	0.16865
36	48.13	0.0115	0.848	16.10	82.27	0.03502	0.16854
38	49.88	0.0116	0.819	16.55	82.49	0.03591	0.16843
40	51.68	0.0116	0.792	17.00	82.71	0.03680	0.16833
42	53.51	0.0116	0.767	17.46	82.93	0.03770	0.16823
44	55.40	0.0117	0.742	17.91	83.15	0.03859	0.16813
46	57.35	0.0117	0.718	18.36	83.36	0.03948	0.16803
48	59.35	0.0117	0.695	18.82	83.57	0.04037	0.16794
50	61.39	0.0118	0.673	19.27	83.78	0.04126	0.16785
52	63.49	0.0118	0.652	19.72	83.99	0.04215	0.16776
54	65.63	0.0118	0.632	20.18	84.20	0.04304	0.16767
56	67.84	0.0119	0.612	20.64	84.41	0.04392	0.16758
58	70.10	0.0119	0.593	21.11	84.62	0.04480	0.16749
60	72.41	0.0119	0.575	21.57	84.82	0.04568	0.16741
62	74.77	0.0120	0.557	22.03	85.02	0.04657	0.16733
64	77.20	0.0120	0.540	22.49	85.22	0.04745	0.16725
66	79.67	0.0120	0.524	22.95	85.42	0.04833	0.16717
68	82.24	0.0121	0.508	23.42	85.62	0.04921	0.16709
70	84.82	0.0121	0.493	23.90	85.82	0.05009	0.16701
72	87.50	0.0121	0.479	24.37	86.02	0.05097	0.16693
74	90.20	0.0122	0.464	24.84	86.22	0.05185	0.16685
76	93.00	0.0122	0.451	25.32	86.42	0.05272	0.16677
78	95.85	0.0122	0.438	25.80	86.61	0.05359	0.16669
80	98.76	0.0123	0.425	26.28	86.80	0.05446	0.16662
82	101.7	0.0123	0.413	26.76	86.99	0.05534	0.16655
84	104.8	0.0124	0.401	27.24	87.18	0.05621	0.16648
86	107.9	0.0124	0.389	27.72	87.37	0.05708	0.16640
88	111.1	0.0124	0.378	28.21	87.56	0.05795	0.16632
90	114.3	0.0125	0.368	28.79	87.74	0.05882	0.16624
92	117.7	0.0125	0.357	29.19	87.92	0.05969	0.16616
94	121.0	0.0125	0.347	29.68	88.10	0.06056	0.16608
96	124.5	0.0126	0.338	30.18	88.28	0.06143	0.16600
98	128.0	0.0126	0.328	30.67	88.45	0.06230	0.16592
100	131.6	0.0127	0.319	31.16	88.62	0.06316	0.16584
110	150.7	0.0129	0.277	33.65	89.43	0.06749	0.16542
120	171.8	0.0131	0.240	36.16	90.15	0.07180	0.16495

<sup>1</sup> Adapted from "Refrigerating Data Book."



Entropy  
1.0



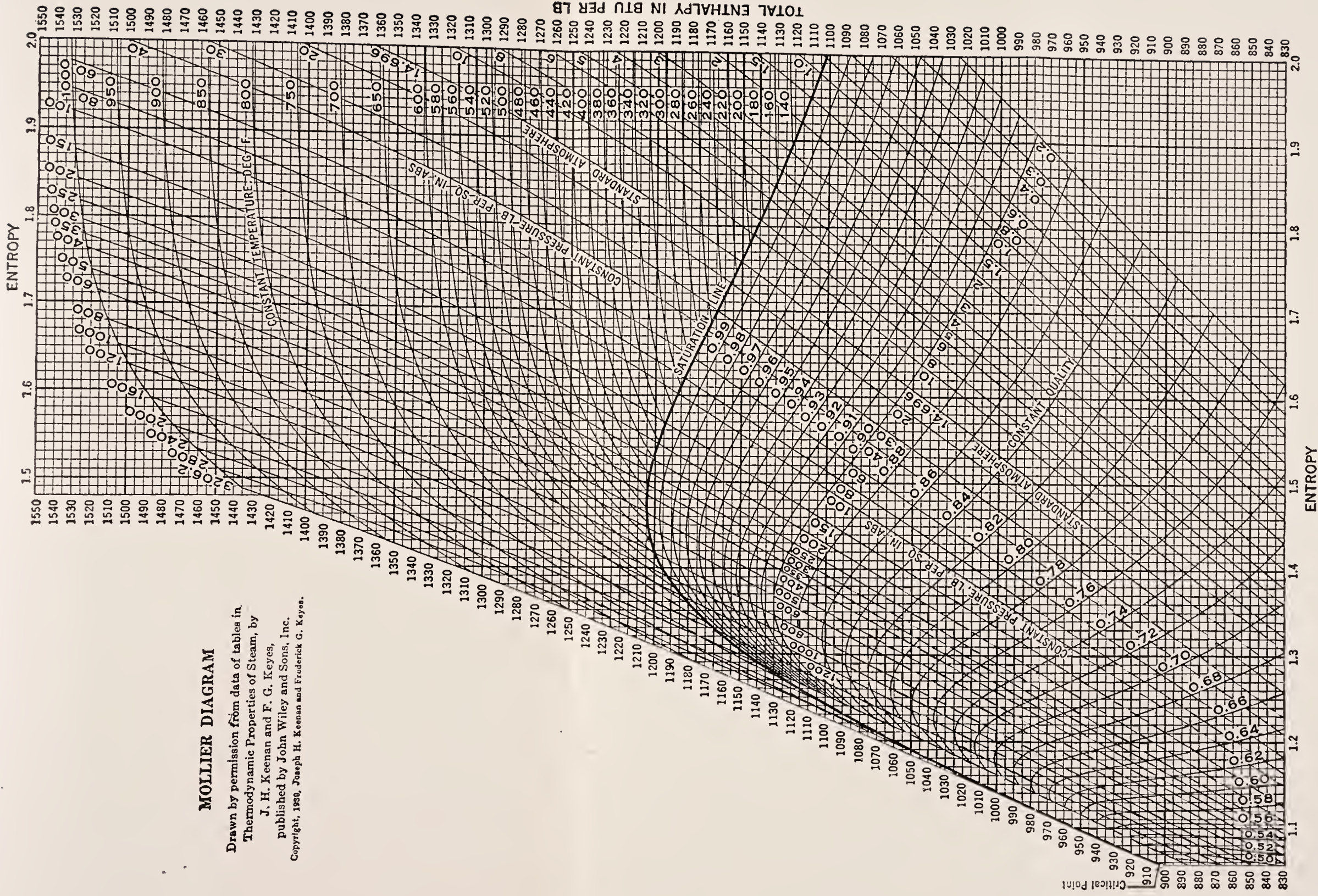




# APPENDIX

## MOLLIER DIAGRAM

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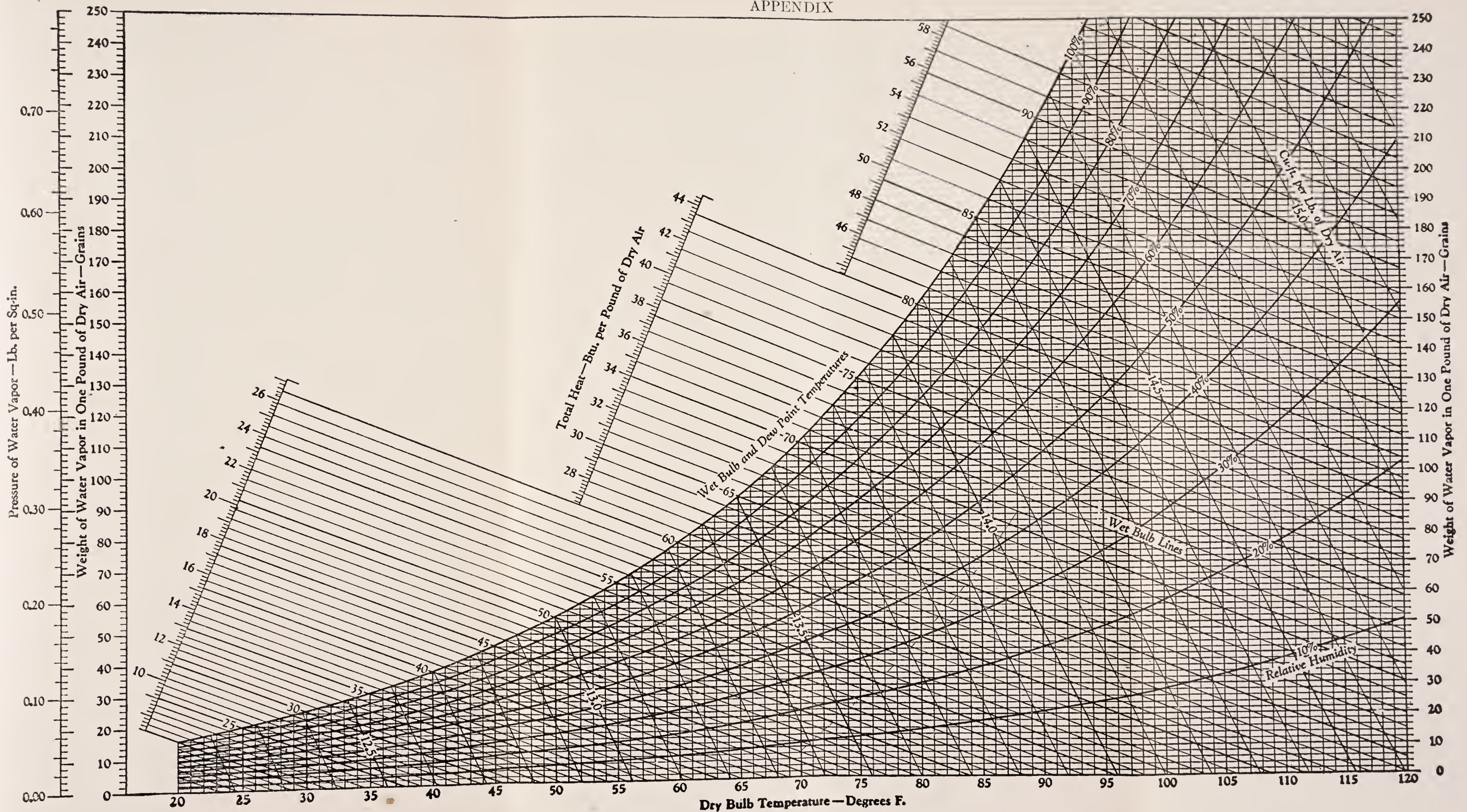


PLATE 3. Psychrometric chart. (Copyright 1942, General Electric Company; reproduced by special permission.)







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